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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 :
C11D 3/395, C07D 213/38, C07F 15/02, 13/00, D06L 3/02, C07D 235/30, 405/14

A1

(11) International Publication Number: WO 00/60043

(43) International Publication Date: 12 October 2000 (12.10.00)

(21) International Application Number: PCT/EP00/02587

(22) International Filing Date: 22 March 2000 (22.03.00)

(30) Priority Data:

9907713.3	1 April 1999 (01.04.99)	GB
9907714.1	1 April 1999 (01.04.99)	GB
PCT/GB99/02876	1 September 1999 (01.09.99)	GB
PCT/GB99/02878	1 September 1999 (01.09.99)	GB
0004858.7	29 February 2000 (29.02.00)	GB

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(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: COMPOSITION AND METHOD FOR BLEACHING A SUBSTRATE

(57) Abstract

The invention relates to catalytically bleaching substrates, especially laundry fabrics, with atmospheric oxygen or air. A method of bleaching a substrate is provided that comprises applying to the substrate, in an aqueous medium, a specified ligand from a selected class which forms a complex with a transition metal, the complex catalysing bleaching of the substrate by atmospheric oxygen. Also provided is an aqueous bleaching composition substantially devoid of peroxygen bleach or a peroxy–based or –generating bleach system. Also provided is a method of treating a textile such as a laundry fabric whereby a complex catalyses bleaching of the textile by atmospheric oxygen after the treatment. The ligand may be used in dry form, or in a liquor that is then dried, such as an aqueous spray–on fabric treatment fluid or a wash liquor for laundry cleaning, or a non–aqueous dry cleaning fluid or spray–on aerosol fluid. The method can confer cleaning benefits to the textile after the treatment. Also provided is a dry textile having a catalyst applied or deposited thereon, whereby bleaching by atmospheric oxygen is catalysed on the textile.

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COMPOSITION AND METHOD FOR BLEACHING A SUBSTRATE

This invention relates to compositions and methods for catalytically bleaching substrates with atmospheric oxygen, more particularly using a defined class of ligand or complex as catalyst, and further relates to ligands and complexes useful in such compositions and methods. This invention also relates to a method of treating textiles, such as laundry fabrics, using the defined class of ligand or complex as catalyst, more specifically to a method whereby bleaching by atmospheric oxygen is catalysed after the treatment.

Peroxygen bleaches are well known for their ability to remove stains from substrates. Traditionally, the substrate is subjected to hydrogen peroxide, or to substances which can generate hydroperoxyl radicals, such as inorganic or organic peroxides. Generally, these systems must be activated. One method of activation is to employ wash temperatures of 60°C or higher. However, these high temperatures often lead to inefficient cleaning, and can also cause premature damage to the substrate.

A preferred approach to generating hydroperoxyl bleach radicals is the use of inorganic peroxides coupled with organic precursor compounds. These systems are employed for many commercial laundry powders. For example, various European systems are based on tetraacetyl ethylenediamine (TAED) as the organic precursor coupled with sodium perborate or sodium percarbonate, whereas in the United States laundry bleach products are typically based on sodium nonanoyloxybenzenesulfonate (SNOBS) as the organic precursor coupled with sodium perborate.

Precursor systems are generally effective but still exhibit several disadvantages. For example, organic precursors are moderately sophisticated molecules requiring multi-step

manufacturing processes resulting in high capital costs. Also, precursor systems have large formulation space requirements so that a significant proportion of a laundry powder must be devoted to the bleach components, leaving less room for other active ingredients and complicating the development of concentrated powders. Moreover, precursor systems do not bleach very efficiently in countries where consumers have wash habits entailing low dosage, short wash times, cold temperatures and low wash liquor to substrate ratios.

Alternatively, or additionally, hydrogen peroxide and peroxy systems can be activated by bleach catalysts, such as by complexes of iron and the ligand N4Py (*i.e.* N, N-bis(pyridin-2-yl-methyl)-bis(pyridin-2-yl)methylamine) disclosed in WO95/34628, or the ligand Tpen (*i.e.* N, N, N', N'-tetra(pyridin-2-yl-methyl)ethylenediamine) disclosed in WO97/48787. According to these publications, molecular oxygen may be used as the oxidant as an alternative to peroxide generating systems. However, no role in catalysing bleaching by atmospheric oxygen in an aqueous medium is reported.

It has long been thought desirable to be able to use atmospheric oxygen (air) as the source for a bleaching species, as this would avoid the need for costly hydroperoxyl generating systems. Unfortunately, air as such is kinetically inert towards bleaching substrates and exhibits no bleaching ability. Recently some progress has been made in this area. For example, WO 97/38074 reports the use of air for oxidising stains on fabrics by bubbling air through an aqueous solution containing an aldehyde and a radical initiator. A broad range of aliphatic, aromatic and heterocyclic aldehydes is reported to be useful, particularly para-substituted aldehydes such as 4-methyl-, 4-ethyl- and 4-isopropyl benzaldehyde, whereas the range of initiators disclosed includes N-hydroxysuccinimide, various peroxides and transition metal coordination complexes.

However, although this system employs molecular oxygen from the air, the aldehyde component and radical initiators such as peroxides are consumed during the bleaching process. These components must therefore be included in the composition in relatively high amounts so as not to become depleted before completion of the bleaching process

in the wash cycle. Moreover. the spent components represent a waste of resources as they can no longer participate in the bleaching process.

Accordingly, it would be desirable to be able to provide a bleaching system based on atmospheric oxygen or air that does not rely primarily on hydrogen peroxide or a hydroperoxyl generating system, and that does not require the presence of organic components such as aldehydes that are consumed in the process. Moreover. it would be desirable to provide such a bleaching system that is effective in aqueous medium.

It may also be noted that the known art teaches a bleaching effect only as long as the substrate is being subjected to the bleaching treatment. Thus, there is no expectation that hydrogen peroxide or peroxy bleach systems could continue to provide a bleaching effect on a treated substrate, such as a laundry fabric after washing and drying. since the bleaching species themselves or any activators necessary for the bleaching systems would be assumed to be removed from the substrate, or consumed or deactivated, on completing the wash cycle and drying.

It would be therefore also be desirable to be able to treat a textile such that, after the treatment is completed, a bleaching effect is observed on the textile. Furthermore, it would be desirable to be able to provide a bleach treatment for textiles such as laundry fabrics whereby residual bleaching occurs when the treated fabric has been treated and is dry.

We have found that a selected class of ligand or complex is surprisingly effective in catalysing the bleaching of substrates using atmospheric oxygen or air. Furthermore, we have found certain novel ligands which are useful in the bleaching of substrates using atmospheric oxygen or air.

Accordingly, in a first aspect, the present invention provides a bleaching composition comprising, in an aqueous medium, atmospheric oxygen and a ligand which forms a complex with a transition metal, the complex catalysing bleaching of a substrate by the

atmospheric oxygen, wherein the aqueous medium is substantially devoid of peroxygen bleach or a peroxy-based or -generating bleach system. The medium is therefore preferably insensitive or stable to catalase. which acts on peroxy species.

In a second aspect. the present invention provides a method of bleaching a substrate comprising applying to the substrate, in an aqueous medium. a ligand which forms a complex with a transition metal, the complex catalysing bleaching of the substrate by atmospheric oxygen.

Furthermore, in a third aspect, the present invention provides the use of a ligand which forms a complex with a transition metal as a catalytic bleaching agent for a substrate in an aqueous medium substantially devoid of peroxygen bleach or a peroxy-based or -generating bleach system, the complex catalysing bleaching of the substrate by the atmospheric oxygen.

We have also found that certain ligands or complexes of this class are surprisingly effective in catalysing bleaching of the substrate by atmospheric oxygen after treatment of the substrate.

Accordingly, in a fourth aspect, the present invention provides a method of treating a textile by contacting the textile with a ligand which forms a complex with a transition metal, whereby the complex catalyses bleaching of the textile by atmospheric oxygen after the treatment.

In a fifth aspect, the present invention provides a dry textile having a ligand as defined above applied or deposited thereon, whereby bleaching by atmospheric oxygen is catalysed on the textile.

In further aspects, the present invention provides ligands and complexes, as defined further below.

Advantageously, the method according to the present invention permits all or the majority of the bleaching species in the medium (on an equivalent weight basis) to be derived from atmospheric oxygen. Thus, the medium can be made wholly or substantially devoid of peroxygen bleach or a peroxy-based or -generating bleach system. Furthermore, the complex is a catalyst for the bleaching process and, as such, is not consumed but can continue to participate in the bleaching process. The catalytically activated bleaching system of the type in accordance with the present invention, which is based on atmospheric oxygen, is therefore both cost-effective and environmentally friendly. Moreover, the bleaching system is operable under unfavourable wash conditions which include low temperatures, short contact times and low dosage requirements. Furthermore, the method is effective in an aqueous medium and is therefore particularly applicable to bleaching of laundry fabrics. Therefore, whilst the composition and method according to the present invention may be used for bleaching any suitable substrate, the preferred substrate is a laundry fabric. The bleaching method may be carried out by simply leaving the substrate in contact with the medium for a sufficient period of time. Preferably, however, the aqueous medium on or containing the substrate is agitated.

An advantage of the method according to the fourth aspect of the invention is that, by enabling a bleaching effect even after the textile has been treated, the benefits of bleaching can be prolonged on the textile. Furthermore, since a bleaching effect is conferred to the textile after the treatment, the treatment itself, such as a laundry wash cycle, may for example be shortened. Moreover, since a bleaching effect is achieved by atmospheric oxygen after treatment of the textile, hydrogen peroxide or peroxy-based bleach systems can be omitted from the treatment substance.

The ligand may be present as a preformed complex of a ligand and a transition metal. Alternatively, the composition may comprise a free ligand that complexes with a transition metal already present in the water or that complexes with a transition metal present in the substrate. The composition may also be formulated as a composition of a

free ligand or a transition metal-substitutable metal-ligand complex. and a source of transition metal, whereby the complex is formed *in situ* in the medium.

The ligand forms a complex with one or more transition metals. in the latter case for example as a dinuclear complex. Suitable transition metals include for example: manganese in oxidation states II-V, iron II-V, copper I-III, cobalt I-III. titanium II-IV. tungsten IV-VI, vanadium II-V and molybdenum II-VI.

The ligand forms a complex of the general formula (A1):

$$[M_aL_kX_n]Y_m \qquad (A1)$$

in which:

M represents a metal selected from Mn(II)-(III)-(IV)-(V). Cu(I)-(II)-(III), Fe(II)-(III)-(IV)-(V), Co(I)-(II)-(III), Ti(II)-(III)-(IV), V(II)-(III)-(IV)-(V), Mo(II)-(III)-(IV)-(V)-(VI) and W(IV)-(V)-(VI), preferably selected from Fe(II)-(III)-(IV)-(V);

L represents a ligand as herein defined. or its protonated or deprotonated analogue;

X represents a coordinating species selected from any mono. bi or tri charged anions and any neutral molecules able to coordinate the metal in a mono, bi or tridentate manner, preferably selected from O^{2-}, RBO_2^{2-}, $RCOO^-$, $RCONR^-$, OH^-, NO_3^-, NO, S^{2-}, RS^-, PO_4^{3-}, PO_3OR^{3-}, H_2O, CO_3^{2-}, HCO_3^-, ROH, $N(R)_3$, ROO^-, O_2^{2-}, O_2^-, RCN, Cl^-, Br^-, OCN^-, SCN^-, CN^-, N_3^-, F^-, I^-, RO^-, ClO_4^-, and $CF_3SO_3^-$, and more preferably selected from O^{2-}, RBO_2^{2-}, $RCOO^-$, OH^-, NO_3^-, S^{2-}, RS^-, PO_3^{4-}, H_2O, CO_3^{2-}, HCO_3^-, ROH, $N(R)_3$, Cl^-, Br^-, OCN^-, SCN^-, RCN, N_3^-, F^-, I^-, RO^-, ClO_4^-, and $CF_3SO_3^-$;

Y represents any non-coordinated counter ion, preferably selected from ClO_4^-, BR_4^-, $[MX_4]^-$, $[MX_4]^{2-}$, PF_6^-, $RCOO^-$, NO_3^-, RO^-, $N^+(R)_4$, ROO^-, O_2^{2-}, O_2^-, Cl^-, Br^-, F^-, I^-, $CF_3SO_3^-$, $S_2O_6^{2-}$, OCN^-, SCN^-, H_2O, RBO_2^{2-}, BF_4^- and BPh_4^-, and more preferably selected from ClO_4^-, BR_4^-, $[FeCl_4]^-$, PF_6^-, $RCOO^-$, NO_3^-, RO^-, $N^+(R)_4$, Cl^-, Br^-, F^-, I^-, $CF_3SO_3^-$, $S_2O_6^{2-}$, OCN^-, SCN^-, H_2O and BF_4^-;

a represents an integer from 1 to 10, preferably from 1 to 4;

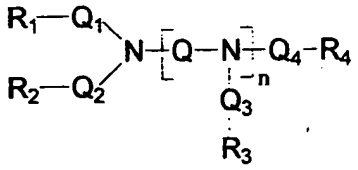
k represents an integer from 1 to 10;

n represents an integer from 1 to 10, preferably from 1 to 4;

m represents zero or an integer from 1 to 20, preferably from 1 to 8; and

each R independently represents a group selected from hydrogen, hydroxyl, -R' and -OR', wherein R'= alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl or a carbonyl derivative group, R' being optionally substituted by one or more functional groups E, wherein E independently represents a functional group selected from -F, -Cl, -Br, -I, -OH, -OR', $-NH_2$, -NHR', $-N(R')_2$, $-N(R')_3^+$, -C(O)R', -OC(O)R', -COOH, $-COO^-(Na^+, K^+)$, -COOR', $-C(O)NH_2$, -C(O)NHR', $-C(O)N(R')_2$, heteroaryl, -R', -SR', -SH, $-P(R')_2$, $-P(O)(R')_2$, $-P(O)(OH)_2$, $-P(O)(OR')_2$, $-NO_2$, $-SO_3H$, $-SO_3^-(Na^+, K^+)$, $-S(O)_2R'$, -NHC(O)R', and -N(R')C(O)R', wherein R' represents cycloalkyl, aryl, arylalkyl, or alkyl optionally substituted by -F, -Cl, -Br, -I, $-NH_3^+$, $-SO_3H$, $-SO_3^-(Na^+, K^+)$, -COOH, $-COO^-(Na^+, K^+)$, $-P(O)(OH)_2$, or $-P(O)(O^-(Na^+, K^+))_2$, and preferably each R independently represents hydrogen, optionally substituted alkyl or optionally substituted aryl, more preferably hydrogen or optionally substituted phenyl, naphthyl or C_{1-4}-alkyl.

The ligand L is of the general formula (I):



(I)

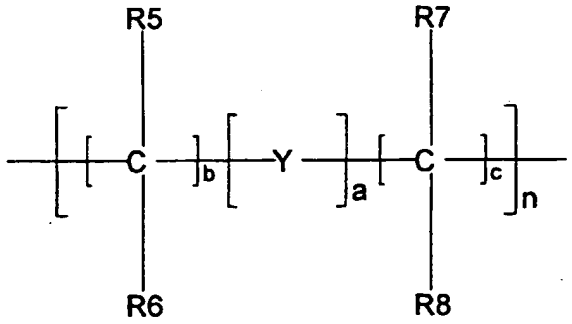
wherein

n = 1 or 2, whereby if n = 2, then each $-Q_3-R_3$ group is independently defined;

R_1, R_2, R_3, R_4 independently represent a group selected from hydrogen, hydroxyl, halogen, $-NH-C(NH)NH_2$, -R and -OR, wherein R= alkyl, alkenyl, cycloalkyl,

heterocycloalkyl, aryl, heteroaryl or a carbonyl derivative group, R being optionally substituted by one or more functional groups E.

Q_1, Q_2, Q_3, Q_4 and Q independently represent a group of the formula:



wherein

$5 \geq a+b+c \geq 1$; a=0-5; b=0-5; c=0-5; n=1 or 2;

Y independently represents a group selected from -O-, -S-, -SO-, $-SO_2-$, -C(O)-, arylene, alkylene, heteroarylene, heterocycloalkylene, -(G)P-, -P(O)- and -(G)N- , wherein G is selected from hydrogen, alkyl, aryl, arylalkyl, cycloalkyl, each except hydrogen being optionally substituted by one or more functional groups E;

R5, R6, R7, R8 independently represent a group selected from hydrogen, hydroxyl, halogen, -R and -OR, wherein R represents alkyl, alkenyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl or a carbonyl derivative group, R being optionally substituted by one or more functional groups E,

or R5 together with R6, or R7 together with R8, or both, represent oxygen,

or R5 together with R7 and/or independently R6 together with R8, or R5 together with R8 and/or independently R6 together with R7, represent C_{1-6}-alkylene optionally substituted by C_{1-4}-alkyl, -F, -Cl, -Br or -I,

provided that at least two of R_1, R_2, R_3, R_4 comprise coordinating heteroatoms and no more than six heteroatoms are coordinated to the same transition metal atom.

At least two, and preferably at least three, of R_1, R_2, R_3, R_4 independently represent a group selected from carboxylate, amido, -NH-C(NH)NH_2, hydroxyphenyl, an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole.

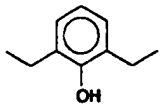
Preferably, substituents for groups R_1, R_2, R_3, R_4, when representing a heterocyclic or heteroaromatic ring, are selected from C_{1-4}-alkyl, aryl, arylalkyl, heteroaryl, methoxy, hydroxy, nitro, amino, carboxyl, halo, and carbonyl.

The groups R5, R6, R7, R8 preferably independently represent a group selected from -H, hydroxy-C_0-C_{20}-alkyl, halo-C_0-C_{20}-alkyl, nitroso, formyl-C_0-C_{20}-alkyl, carboxyl-C_0-C_{20}-alkyl and esters and salts thereof, carbamoyl-C_0-C_{20}-alkyl, sulfo-C_0-C_{20}-alkyl and esters and salts thereof, sulfamoyl-C_0-C_{20}-alkyl, amino-C_0-C_{20}-alkyl, aryl-C_0-C_{20}-alkyl, C_0-C_{20}-alkyl, alkoxy-C_0-C_8-alkyl, carbonyl-C_0-C_6-alkoxy, and C_0-C_{20}-alkylamide. Preferably, none of R6-R8 is linked together.

The groups Q_1, Q_2, Q_3, Q_4 preferably independently represent a group selected from -CH_2- and -CH_2CH_2-.

Group Q is preferably a group selected from -$(CH_2)_{2-4}$-, -$CH_2CH(OH)CH_2$-,

 optionally substituted by methyl or ethyl,



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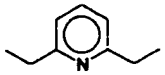

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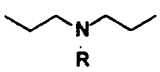
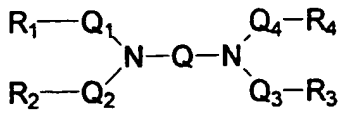


wherein R represents -H or C_{1-4}-alkyl.

Preferably, Q_1, Q_2, Q_3, Q_4 are defined such that a=b=0, c=1 and n=1, and Q is defined such that a=b=0, c=2 and n=1.

In a first preferred embodiment, the ligand L is of the general formula (II):



(II)

wherein

Q_1, Q_2, Q_3, Q_4 are defined such that a=b=0, c=1 or 2 and n=1;

Q is defined such that a=b=0, c=2,3 or 4 and n=1; and

R_1, R_2, R_3, R_4, R7, R8 are independently defined as for formula (I).

Preferred classes of ligands according to the first preferred embodiment, as represented by formula (II) above, are as follows:

(i) ligands of the general formula (II) wherein:

R_1, R_2, R_3, R_4 each independently represent a coordinating group selected from carboxylate, amido, -NH-C(NH)NH_2, hydroxyphenyl, an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole.

In this class, we prefer that:

Q is defined such that a=b=0, c=2 or 3 and n=1;

R_1, R_2, R_3, R_4 each independently represent a coordinating group selected from optionally substituted pyridin-2-yl, optionally substituted imidazol-2-yl, optionally substituted imidazol-4-yl, optionally substituted pyrazol-1-yl, and optionally substituted quinolin-2-yl.

(ii) ligands of the general formula (II) wherein:

R_1, R_2, R_3 each independently represent a coordinating group selected from carboxylate, amido, -NH-C(NH)NH_2, hydroxyphenyl, an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole; and

R_4 represents a group selected from hydrogen, C_{1-20} optionally substituted alkyl, C_{1-20} optionally substituted arylalkyl, aryl, and C_{1-20} optionally substituted NR_3^+ (wherein R=C_{1-8}-alkyl).

In this class, we prefer that:

Q is defined such that a=b=0, c=2 or 3 and n=1;

R_1, R_2, R_3 each independently represent a coordinating group selected from optionally substituted pyridin-2-yl, optionally substituted imidazol-2-yl, optionally substituted imidazol-4-yl, optionally substituted pyrazol-1-yl, and optionally substituted quinolin-2-yl; and

R_4 represents a group selected from hydrogen, C_{1-10} optionally substituted alkyl, C_{1-5}-furanyl, C_{1-5} optionally substituted benzylalkyl, benzyl, C_{1-5} optionally substituted alkoxy, and C_{1-20} optionally substituted N^+Me_3.

(iii) ligands of the general formula (II) wherein:

R_1, R_4 each independently represent a coordinating group selected from carboxylate, amido, -NH-C(NH)NH_2, hydroxyphenyl, an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole; and

R_2, R_3 each independently represent a group selected from hydrogen, C_{1-20} optionally substituted alkyl, C_{1-20} optionally substituted arylalkyl, aryl, and C_{1-20} optionally substituted NR_3^+ (wherein R=C_{1-8}-alkyl).

In this class, we prefer that:

Q is defined such that a=b=0, c=2 or 3 and n=1:

R_1, R_4 each independently represent a coordinating group selected from optionally substituted pyridin-2-yl, optionally substituted imidazol-2-yl, optionally substituted imidazol-4-yl, optionally substituted pyrazol-1-yl, and optionally substituted quinolin-2-yl; and

R_2, R_3 each independently represent a group selected from hydrogen, C_{1-10} optionally substituted alkyl, C_{1-5}-furanyl, C_{1-5} optionally substituted benzylalkyl, benzyl, C_{1-5} optionally substituted alkoxy, and C_{1-20} optionally substituted N^+Me_3.

The counter ions Y in formula (A1) balance the charge z on the complex formed by the ligand L, metal M and coordinating species X. Thus, if the charge z is positive, Y may be an anion such as $RCOO^-$, BPh_4^-, ClO_4^-, BF_4^-, PF_6^-, RSO_3^-, RSO_4^-, SO_4^{2-}, NO_3^-, F^-, Cl^-, Br^-, or I^-, with R being hydrogen, optionally substituted alkyl or optionally substituted aryl. If z is negative, Y may be a common cation such as an alkali metal, alkaline earth metal or (alkyl)ammonium cation.

In a second preferred embodiment, the ligand forms a complex of the general formula (I) as defined above, but wherein L represents a pentadentate or hexadentate ligand of general formula (III):

$$R^1R^1N\text{-}W\text{-}NR^1R^2$$

wherein

each R^1 independently represents $-R^3-V$, in which R^3 represents optionally substituted alkylene, alkenylene, oxyalkylene, aminoalkylene or alkylene ether, and V represents an optionally substituted heteroaryl group selected from pyridinyl, pyrazinyl, pyrazolyl, pyrrolyl, imidazolyl, benzimidazolyl, pyrimidinyl, triazolyl and thiazolyl;

W represents an optionally substituted alkylene bridging group selected from $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-CH_2CH_2CH_2CH_2-$, $-CH_2-C_6H_4-CH_2-$, $-CH_2-C_6H_{10}-CH_2-$, and $-CH_2-C_{10}H_6-CH_2-$; and

R^2 represents a group selected from R^1, and alkyl, aryl and arylalkyl groups optionally substituted with a substituent selected from hydroxy, alkoxy, phenoxy, carboxylate, carboxamide, carboxylic ester, sulfonate, amine, alkylamine and $N^+(R^4)_3$, wherein R^4 is selected from hydrogen, alkanyl, alkenyl, arylalkanyl, arylalkenyl, oxyalkanyl, oxyalkenyl, aminoalkanyl, aminoalkenyl, alkanyl ether and alkenyl ether.

The ligand L having the general formula (III), as defined above, is a pentadentate ligand or, if R^1=R^2, can be a hexadentate ligand. As mentioned above, by 'pentadentate' is meant that five hetero atoms can coordinate to the metal M ion in the metal-complex. Similarly, by 'hexadentate' is meant that six hetero atoms can in principle coordinate to the metal M ion. However, in this case it is believed that one of the arms will not be bound in the complex, so that the hexadentate ligand will be penta coordinating.

In the formula (III), two hetero atoms are linked by the bridging group W and one coordinating hetero atom is contained in each of the three R^1 groups. Preferably, the coordinating hetero atoms are nitrogen atoms.

The ligand L of formula (III) comprises at least one optionally substituted heteroaryl group in each of the three R^1 groups. Preferably, the heteroaryl group is a pyridin-2-yl group, in particular a methyl- or ethyl-substituted pyridin-2-yl group. The heteroaryl group is linked to an N atom in formula (III), preferably *via* an alkylene group, more preferably a methylene group. Most preferably, the heteroaryl group is a 3-methyl-pyridin-2-yl group linked to an N atom *via* methylene.

The group R^2 in formula (III) is a substituted or unsubstituted alkyl, aryl or arylalkyl group, or a group R^1. However, preferably R^2 is different from each of the groups R^1 in the formula above. Preferably, R^2 is methyl, ethyl, benzyl, 2-hydroxyethyl or 2-methoxyethyl. More preferably, R^2 is methyl or ethyl.

The bridging group W may be a substituted or unsubstituted alkylene group selected from $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-CH_2CH_2CH_2CH_2-$, $-CH_2-C_6H_4-CH_2-$, $-CH_2-C_6H_{10}-$

CH_2-, and -CH_2-$C_{10}H_6$-CH_2- (wherein -C_6H_4-, -C_6H_{10}-, -$C_{10}H_6$- can be *ortho*-, *para*-, or *meta*-C_6H_4-, -C_6H_{10}-, -$C_{10}H_6$-). Preferably, the bridging group W is an ethylene or 1,4-butylene group, more preferably an ethylene group.

Preferably, V represents substituted pyridin-2-yl, especially methyl-substituted or ethyl-substituted pyridin-2-yl, and most preferably V represents 3-methyl pyridin-2-yl.

Suitable counter ions Y include those which give rise to the formation of storage-stable solids. Preferred counter ions for the preferred metal complexes are selected from R^7COO^-, ClO_4^-, BF_4^-, PF_6^-, RSO_3^- (in particular $CF_3SO_3^-$), RSO_4^-, SO_4^{2-}, NO_3^-, F^-, Cl^-, Br^-, and I^-, wherein R represents hydrogen or optionally substituted phenyl, naphthyl or C_1-C_4 alkyl.

It will be appreciated that the complex (A1) can be formed by any appropriate means, including *in situ* formation whereby precursors of the complex are transformed into the active complex of general formula (A1) under conditions of storage or use. Preferably, the complex is formed as a well-defined complex or in a solvent mixture comprising a salt of the metal M and the ligand L or ligand L-generating species. Alternatively, the catalyst may be formed *in situ* from suitable precursors for the complex, for example in a solution or dispersion containing the precursor materials. In one such example, the active catalyst may be formed *in situ* in a mixture comprising a salt of the metal M and the ligand L, or a ligand L-generating species, in a suitable solvent. Thus, for example, if M is iron, an iron salt such as $FeSO_4$ can be mixed in solution with the ligand L, or a ligand L-generating species, to form the active complex. Thus, for example, the composition may formed from a mixture of the ligand L and a metal salt MX_n in which preferably n=1-5, more preferably 1-3. In another such example, the ligand L, or a ligand L-generating species, can be mixed with metal M ions present in the substrate or wash liquor to form the active catalyst *in situ*. Suitable ligand L-generating species include metal-free compounds or metal coordination complexes that comprise the ligand L and can be substituted by metal M ions to form the active complex according the formula (A1).

Accordingly, in alternative second preferred embodiment. the complex is a compound of the general formula (IIIa):

$$[\{M'_aL\}_bX_c]^zY_q$$

in which

M' represents hydrogen or a metal selected from Ti, V, Co, Zn, Mg, Ca, Sr, Ba, Na, K, and Li;

X represents a coordinating species;

a represents an integer in the range from 1 to 5;

b represents an integer in the range from 1 to 4;

c represents zero or an integer in the range from 0 to 5;

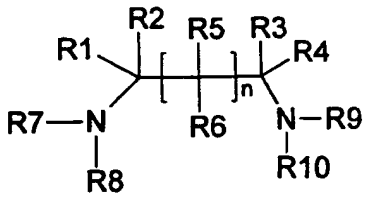
z represents the charge of the compound and is an integer which can be positive, zero or negative;

Y represents a counter ion, the type of which is dependent on the charge of the compound;

q = z/[charge Y]; and

L represents a pentadentate ligand of general formula (III) as defined above.

In a third embodiment, the ligand L has the general formula (IV):



(IV)

wherein groups R1, R2, R3, R4, R5 are -H or C_0-C_{20}-alkyl, n=0 or 1, R6 is -H, alkyl, -OH or -SH, and R7, R8, R9, R10 are each independently selected from -H, C_0-C_{20}-alkyl, heteroaryl-C_0-C_{20}-alkyl, alkoxy-C_0-C_8-alkyl and amino- C_0-C_{20}-alkyl.

Examples of preferred ligands in their simplest forms are:

N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine;
N-trimethylammoniumpropyl-N,N',N'-tris(pyridin-2-ylmethyl)-ethylenediamine;
N-(2-hydroxyethylene)-N,N',N'-tris(pyridin-2-ylmethyl)-ethylenediamine;
N,N,N',N'-tetrakis(3-methyl-pyridin-2-ylmethyl)-ethylene-diamine;
N,N'-dimethyl-N,N'-bis(pyridin-2-ylmethyl)-cyclohexane-1,2-diamine;
N-(2-hydroxyethylene)-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine;
N-methyl-N,N',N'-tris(pyridin-2-ylmethyl)-ethylenediamine;
N-methyl-N,N',N'-tris(5-ethyl-pyridin-2-ylmethyl)-ethylenediamine;
N-methyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)-ethylenediamine;
N-methyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine;
N-benzyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine;
N-ethyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine;
N,N,N'-tris(3-methyl-pyridin-2-ylmethyl)-N'(2'-methoxy-ethyl-1)-ethylenediamine;
N,N,N'-tris(1-methyl-benzimidazol-2-yl)-N'-methyl-ethylenediamine;
N-(furan-2-yl)-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine;
N-(2-hydroxyethylene)-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)-ethylenediamine;

N-methyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-ethyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-benzyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-(2-hydroxyethyl)-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-(2-methoxyethyl)-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;

N-methyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-ethyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;

N-benzyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-(2-hydroxyethyl)-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-(2-methoxyethyl)-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;

N-methyl-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-ethyl-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-benzyl-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-(2-hydroxyethyl)-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-(2-methoxyethyl)-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;

N-methyl-N,N',N'-tris(5-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-ethyl-N,N',N'-tris(5-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-benzyl-N,N',N'-tris(5-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine; and
N-(2-methoxyethyl)-N,N',N'-tris(5-ethyl-pyridin-2-ylmethyl)ethylene-1,2-diamine.

More preferred ligands are:
N-methyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-ethyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-benzyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
N-(2-hydroxyethyl)-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine;
and
N-(2-methoxyethyl)-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)ethylene-1,2-diamine.

The bleaching compositions according to the present invention may be used for laundry cleaning, hard surface cleaning (including cleaning of lavatories, kitchen work surfaces, floors, mechanical ware washing etc.). As is generally known in the art, bleaching compositions are also employed in waste-water treatment, pulp bleaching during the manufacture of paper, leather manufacture, dye transfer inhibition, food processing, starch bleaching, sterilisation, whitening in oral hygiene preparations and/or contact lens disinfection.

In the context of the present invention bleaching should be understood as relating generally to the decolourisation of stains or of other materials attached to or associated with a substrate. However. it is envisaged that the present invention can be applied where a requirement is the removal and/or neutralisation by an oxidative bleaching reaction of malodours or other undesirable components attached to or otherwise associated with a substrate. Furthermore. in the context of the present invention bleaching is to be understood as being restricted to any bleaching mechanism or process that does not require the presence of light or activation by light. Thus. photobleaching compositions and processes relying on the use of photobleach catalysts or photobleach activators and the presence of light are excluded from the present invention.

In typical washing compositions the level of the catalyst is such that the in-use level is from 0.05μM to 50mM, with preferred in-use levels for domestic laundry operations falling in the range 0.5 μM to 100 μM, more preferably from 1 μM to 10 μM. Higher levels may be desired and applied in industrial bleaching processes, such as textile and paper pulp bleaching.

Preferably, the aqueous medium has a pH in the range from pH 6 to 13, more preferably from pH 6 to 11, still more preferably from pH 8 to 11, and most preferably from pH 8 to 10, in particular from pH 9 to 10.

The bleaching composition of the present invention has particular application in detergent formulations, especially for laundry cleaning. Accordingly, in another preferred embodiment, the present invention provides a detergent bleach composition comprising a bleaching composition as defined above and additionally a surface-active material, optionally together with detergency builder.

The bleach composition according to the present invention may for example contain a surface-active material in an amount of from 10 to 50% by weight. The surface-active material may be naturally derived, such as soap, or a synthetic material selected from anionic, nonionic, amphoteric, zwitterionic, cationic actives and mixtures thereof.

Many suitable actives are commercially available and are fully described in the literature, for example in "Surface Active Agents and Detergents". Volumes I and II. by Schwartz, Perry and Berch.

Typical synthetic anionic surface-actives are usually water-soluble alkali metal salts of organic sulfates and sulfonates having alkyl groups containing from about 8 to about 22 carbon atoms, the term "alkyl" being used to include the alkyl portion of higher aryl groups. Examples of suitable synthetic anionic detergent compounds are sodium and ammonium alkyl sulfates, especially those obtained by sulfating higher (C_8-C_{18}) alcohols produced, for example, from tallow or coconut oil; sodium and ammonium alkyl (C_9-C_{20}) benzene sulfonates, particularly sodium linear secondary alkyl (C_{10}-C_{15}) benzene sulfonates; sodium alkyl glyceryl ether sulfates, especially those ethers of the higher alcohols derived from tallow or coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium and ammonium salts of sulfuric acid esters of higher (C_9-C_{18}) fatty alcohol alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralised with sodium hydroxide; sodium and ammonium salts of fatty acid amides of methyl taurine; alkane monosulfonates such as those derived by reacting alpha-olefins (C_8-C_{20}) with sodium bisulfite and those derived by reacting paraffins with SO_2 and Cl_2 and then hydrolysing with a base to produce a random sulfonate; sodium and ammonium (C_7-C_{12}) dialkyl sulfosuccinates; and olefin sulfonates, which term is used to describe material made by reacting olefins, particularly (C_{10}-C_{20}) alpha-olefins, with SO_3 and then neutralising and hydrolysing the reaction product. The preferred anionic detergent compounds are sodium (C_{10}-C_{15}) alkylbenzene sulfonates, and sodium (C_{16}-C_{18}) alkyl ether sulfates.

Examples of suitable nonionic surface-active compounds which may be used, preferably together with the anionic surface-active compounds, include, in particular, the reaction products of alkylene oxides, usually ethylene oxide, with alkyl (C_6-C_{22}) phenols, generally 5-25 EO, *i.e.* 5-25 units of ethylene oxides per molecule; and the condensation products of aliphatic (C_8-C_{18}) primary or secondary linear or branched alcohols with

ethylene oxide, generally 2-30 EO. Other so-called nonionic surface-actives include alkyl polyglycosides, sugar esters. long-chain tertiary amine oxides. long-chain tertiary phosphine oxides and dialkyl sulfoxides.

Amphoteric or zwitterionic surface-active compounds can also be used in the compositions of the invention but this is not normally desired owing to their relatively high cost. If any amphoteric or zwitterionic detergent compounds are used, it is generally in small amounts in compositions based on the much more commonly used synthetic anionic and nonionic actives.

The detergent bleach composition of the invention will preferably comprise from 1 to 15 % wt of anionic surfactant and from 10 to 40 % by weight of nonionic surfactant. In a further preferred embodiment, the detergent active system is free from C_{16}-C_{12} fatty acid soaps.

The bleach composition of the present invention may also contains a detergency builder, for example in an amount of from about 5 to 80 % by weight. preferably from about 10 to 60 % by weight.

Builder materials may be selected from 1) calcium sequestrant materials, 2) precipitating materials, 3) calcium ion-exchange materials and 4) mixtures thereof.

Examples of calcium sequestrant builder materials include alkali metal polyphosphates, such as sodium tripolyphosphate; nitrilotriacetic acid and its water-soluble salts; the alkali metal salts of carboxymethyloxy succinic acid, ethylene diamine tetraacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, citric acid; and polyacetal carboxylates as disclosed in US-A-4,144,226 and US-A-4,146,495.

Examples of precipitating builder materials include sodium orthophosphate and sodium carbonate.

Examples of calcium ion-exchange builder materials include the various types of water-insoluble crystalline or amorphous aluminosilicates. of which zeolites are the best known representatives. *e.g.* zeolite A. zeolite B (also known as zeolite P). zeolite C. zeolite X. zeolite Y and also the zeolite P-type as described in EP-A-0.384.070.

In particular, the compositions of the invention may contain any one of the organic and inorganic builder materials, though, for environmental reasons, phosphate builders are preferably omitted or only used in very small amounts. Typical builders usable in the present invention are, for example, sodium carbonate, calcite/carbonate. the sodium salt of nitrilotriacetic acid, sodium citrate, carboxymethyloxy malonate, carboxymethyloxy succinate and water-insoluble crystalline or amorphous aluminosilicate builder materials, each of which can be used as the main builder, either alone or in admixture with minor amounts of other builders or polymers as co-builder.

It is preferred that the composition contains not more than 5% by weight of a carbonate builder, expressed as sodium carbonate, more preferably not more than 2.5 % by weight to substantially nil, if the composition pH lies in the lower alkaline region of up to 10.

Apart from the components already mentioned, the bleach composition of the present invention can contain any of the conventional additives in amounts of which such materials are normally employed in fabric washing detergent compositions. Examples of these additives include buffers such as carbonates, lather boosters, such as alkanolamides, particularly the monoethanol amides derived from palmkernel fatty acids and coconut fatty acids; lather depressants, such as alkyl phosphates and silicones; anti-redeposition agents, such as sodium carboxymethyl cellulose and alkyl or substituted alkyl cellulose ethers; stabilisers, such as phosphonic acid derivatives (*i.e.* Dequest® types); fabric softening agents; inorganic salts and alkaline buffering agents, such as sodium sulfate and sodium silicate; and, usually in very small amounts, fluorescent agents; perfumes; enzymes, such as proteases, cellulases, lipases, amylases and oxidases; germicides and colourants.

Transition metal sequestrants such as EDTA. and phosphonic acid derivatives such as EDTMP (ethylene diamine tetra(methylene phosphonate)) may also be included. in addition to the ligand specified, for example to improve the stability sensitive ingredients such as enzymes. fluorescent agents and perfumes. but provided the composition remains bleaching effective. However. the composition according to the present invention containing the ligand, is preferably substantially, and more preferably completely. devoid of transition metal sequestrants (other than the ligand).

Whilst the present invention is based on the catalytic bleaching of a substrate by atmospheric oxygen or air, it will be appreciated that small amounts of hydrogen peroxide or peroxy-based or -generating systems may be included in the composition. if desired. Therefore, by "substantially devoid of peroxygen bleach or peroxy-based or -generating bleach systems" is meant that the composition contains from 0 to 50 %, preferably from 0 to 10 %, more preferably from 0 to 5 %, and optimally from 0 to 2 % by molar weight on an oxygen basis, of peroxygen bleach or peroxy-based or -generating bleach systems. Preferably, however, the composition will be wholly devoid of peroxygen bleach or peroxy-based or -generating bleach systems.

Thus, at least 10 %, preferably at least 50 % and optimally at least 90 % of any bleaching of the substrate is effected by oxygen sourced from the air.

According to the fourth aspect, the catalyst may be contacted to the textile fabric in any suitable manner. For example, it may be applied in dry form, such as in powder form, or in a liquor that is then dried, for example as an aqueous spray-on fabric treatment fluid or a wash liquor for laundry cleaning, or a non-aqueous dry cleaning fluid or spray-on aerosol fluid. Other suitable means of contacting the catalyst to the textile may be used, as further explained below.

Any suitable textile that is susceptible to bleaching or one that one might wish to subject to bleaching may be used. Preferably the textile is a laundry fabric or garment.

The bleaching method of the fourth aspect may be carried out by simply leaving the substrate in contact with the catalyst for a sufficient period of time. Preferably, however, the catalyst is in an aqueous medium, and the aqueous medium on or containing the substrate is agitated.

In a preferred embodiment, the treated textile is dried, by allowing it to dry under ambient temperature or at elevated temperatures.

In a particularly preferred embodiment the method according to the fourth aspect is carried out on a laundry fabric using aqueous treatment liquor. In particular the treatment may be effected in, or as an adjunct to, an essentially conventional wash cycle for cleaning laundry. More preferably, the treatment is carried out in an aqueous detergent wash liquor. The catalyst can be delivered into the wash liquor from a powder, granule, pellet, tablet, block, bar or other such solid form. The solid form can comprise a carrier, which can be particulate, sheet-like or comprise a three-dimensional object. The carrier can be dispersible or soluble in the wash liquor or may remain substantially intact. In other embodiments, the catalyst can be delivered into the wash liquor from a paste, gel or liquid concentrate.

It is particularly advantageous that the catalyst used in the method of the fourth aspect makes use of atmospheric oxygen in its bleaching activity. This avoids the requirement that peroxygen bleaches and/or other relatively large quantities of reactive substances need be used in the treatment process. Consequently, only a relatively small quantity of bleach active substance need be employed and this allows dosage routes to be exploited which could previously not be used. Thus, while it is preferable to include the catalyst in a composition that is normally used in a washing process, such as a pre-treatment, main-wash, conditioning composition or ironing aid, other means for ensuring that the catalyst is present in the wash liquor may be envisaged.

For example, it is envisaged that the catalyst can be presented in the form of a body from which it is slowly released during the whole or part of the laundry process. Such release can occur over the course of a single wash or over the course of a plurality of

washes. In the latter case it is envisaged that the catalyst can be released from a carrier substrate used in association with the wash process, e.g. from a body placed in the dispenser drawer of a washing machine, elsewhere in the delivery system or in the drum of the washing machine. When used in the drum of the washing machine the carrier can be freely moving or fixed relative to the drum. Such fixing can be achieved by mechanical means, for example by barbs that interact with the drum wall, or employ other forces, for example a magnetic force. The modification of a washing machine to provide for means to hold and retain such a carrier is envisaged similar means being known from the analogous art of toilet block manufacture. Freely moving carriers such as shuttles for dosage of surfactant materials and/or other detergent ingredients into the wash can comprise means for the release of the catalyst into the wash.

In the alternative, the catalyst can be presented in the form of a wash additive that preferably is soluble. The additive can take any of the physical forms used for wash additives, including powder, granule, pellet, sheet, tablet, block, bar or other such solid form or take the form of a paste, gel or liquid. Dosage of the additive can be unitary or in a quantity determined by the user. While it is envisaged that such additives can be used in the main washing cycle, the use of them in the conditioning or drying cycle is not hereby excluded.

The present invention is not limited to those circumstances in which a washing machine is employed, but can be applied where washing is performed in some alternative vessel. In these circumstances it is envisaged that the catalyst can be delivered by means of slow release from the bowl, bucket or other vessel which is being employed, or from any implement which is being employed, such as a brush, bat or dolly, or from any suitable applicator.

Suitable pre-treatment means for application of the catalyst to the textile material prior to the main wash include sprays, pens, roller-ball devices, bars, soft solid applicator sticks and impregnated cloths or cloths containing microcapsules. Such means are well known in the analogous art of deodorant application and/or in spot treatment of textiles.

Similar means for application are employed in those embodiments where the catalyst is applied after the main washing and/or conditioning steps have been performed. e.g. prior to or after ironing or drying of the cloth. For example. the catalyst may be applied using tapes, sheets or sticking plasters coated or impregnated with the substance. or containing microcapsules of the substance. The catalyst may for example be incorporated into a drier sheet so as to be activated or released during a tumble-drier cycle, or the substance can be provided in an impregnated or microcapsule-containing sheet so as to be delivered to the textile when ironed.

Throughout the description and claims generic groups have been used. for example alkyl, alkoxy, aryl. Unless otherwise specified the following are preferred group restrictions that may be applied to generic groups found within compounds disclosed herein:

alkyl: linear and branched C1-C8-alkyl,

alkenyl: C2-C6-alkenyl,

cycloalkyl: C3-C8-cycloalkyl,

alkoxy: C1-C6-alkoxy,

alkylene: selected from the group consisting of: methylene; 1,1-ethylene; 1,2-ethylene; 1,1-propylidene; 1,2-propylene; 1,3-propylene; 2,2-propylidene; butan-2-ol-1,4-diyl; propan-2-ol-1,3-diyl; 1,4-butylene; cyclohexane-1,1-diyl; cyclohexan-1,2-diyl; cyclohexan-1,3-diyl; cyclohexan-1,4-diyl; cyclopentane-1,1-diyl; cyclopentan-1,2-diyl; and cyclopentan-1,3-diyl,

aryl: selected from homoaromatic compounds having a molecular weight under 300,

arylene: selected from the group consisting of: 1,2-phenylene; 1,3-phenylene; 1,4-phenylene; 1,2-naphtalenylene; 1,3-naphtalenylene; 1,4-naphtalenylene; 2,3-naphtalenylene; 1-hydroxy-2,3-phenylene; 1-hydroxy-2,4-phenylene; 1-hydroxy-2,5-phenylene; and 1-hydroxy-2,6-phenylene,

heteroaryl: selected from the group consisting of: pyridinyl; pyrimidinyl; pyrazinyl; triazolyl; pyridazinyl; 1,3,5-triazinyl; quinolinyl; isoquinolinyl; quinoxalinyl; imidazolyl; pyrazolyl; benzimidazolyl; thiazolyl; oxazolidinyl; pyrrolyl; carbazolyl; indolyl; and isoindolyl, wherein the heteroaryl may be connected to the compound via any atom in the ring of the selected heteroaryl,

heteroarylene: selected from the group consisting of: pyridindiyl; quinolindiyl; pyrazodiyl; pyrazoldiyl; triazolediyl; pyrazindiyl; and imidazolediyl, wherein the heteroarylene acts as a bridge in the compound via any atom in the ring of the selected heteroarylene, more specifically preferred are: pyridin-2,3-diyl; pyridin-2,4-diyl; pyridin-2,5-diyl; pyridin-2,6-diyl; pyridin-3,4-diyl; pyridin-3,5-diyl; quinolin-2,3-diyl; quinolin-2,4-diyl; quinolin-2,8-diyl; isoquinolin-1,3-diyl; isoquinolin-1,4-diyl; pyrazol-1,3-diyl; pyrazol-3,5-diyl; triazole-3,5-diyl; triazole-1,3-diyl; pyrazin-2,5-diyl; and imidazole-2,4-diyl,

heterocycloalkyl: selected from the group consisting of: pyrrolinyl; pyrrolidinyl; morpholinyl; piperidinyl; piperazinyl; hexamethylene imine; 1,4-piperazinyl; tetrahydrothiophenyl; tetrahydrofuranyl; 1,4,7-triazacyclononanyl; 1,4,8,11-tetraazacyclotetradecanyl; 1,4,7,10,13-pentaazacyclopentadecanyl; 1,4-diaza-7-thia-cyclononanyl; 1,4-diaza-7-oxa-cyclononanyl; 1,4,7,10-tetraazacyclododecanyl; 1,4-dioxanyl; 1,4,7-trithia-cyclononanyl; tetrahydropyranyl; and oxazolidinyl, wherein the heterocycloalkyl may be connected to the compound via any atom in the ring of the selected heterocycloalkyl,

heterocycloalkylene: selected from the group consisting of: piperidin-1,2-ylene; piperidin-2,6-ylene; piperidin-4,4-ylidene; 1,4-piperazin-1,4-ylene; 1,4-piperazin-2,3-

ylene; 1,4-piperazin-2,5-ylene; 1,4-piperazin-2,6-ylene; 1,4-piperazin-1,2-ylene; 1,4-piperazin-1,3-ylene; 1,4-piperazin-1,4-ylene; tetrahydrothiophen-2,5-ylene; tetrahydrothiophen-3,4-ylene; tetrahydrothiophen-2,3-ylene; tetrahydrofuran-2,5-ylene; tetrahydrofuran-3,4-ylene; tetrahydrofuran-2,3-ylene; pyrrolidin-2,5-ylene; pyrrolidin-3,4-ylene; pyrrolidin-2,3-ylene; pyrrolidin-1,2-ylene; pyrrolidin-1,3-ylene; pyrrolidin-2,2-ylidene; 1,4,7-triazacyclonon-1,4-ylene; 1,4,7-triazacyclonon-2,3-ylene; 1,4,7-triazacyclonon-2,9-ylene; 1,4,7-triazacyclonon-3,8-ylene; 1,4,7-triazacyclonon-2,2-ylidene; 1,4,8,11-tetraazacyclotetradec-1,4-ylene; 1,4,8,11-tetraazacyclotetradec-1,8-ylene; 1,4,8,11-tetraazacyclotetradec-2,3-ylene; 1,4,8,11-tetraazacyclotetradec-2,5-ylene; 1,4,8,11-tetraazacyclotetradec-1,2-ylene; 1,4,8,11-tetraazacyclotetradec-2,2-ylidene; 1,4,7,10-tetraazacyclododec-1,4-ylene; 1,4,7,10-tetraazacyclododec-1,7-ylene; 1,4,7,10-tetraazacyclododec-1,2-ylene; 1,4,7,10-tetraazacyclododec-2,3-ylene; 1,4,7,10-tetraazacyclododec-2,2-ylidene; 1,4,7,10,13-pentaazacyclopentadec-1,4-ylene; 1,4,7,10,13-pentaazacyclopentadec-1,7-ylene; 1,4,7,10,13-pentaazacyclopentadec-2,3-ylene; 1,4,7,10,13-pentaazacyclopentadec-1,2-ylene; 1,4,7,10,13-pentaazacyclopentadec-2,2-ylidene; 1,4-diaza-7-thia-cyclonon-1,4-ylene; 1,4-diaza-7-thia-cyclonon-1,2-ylene; 1,4-diaza-7-thia-cyclonon-2,3-ylene; 1,4-diaza-7-thia-cyclonon-6,8-ylene; 1,4-diaza-7-thia-cyclonon-2,2-ylidene; 1,4-diaza-7-oxa-cyclonon-1,4-ylene; 1,4-diaza-7-oxa-cyclonon-1,2-ylene; 1,4-diaza-7-oxa-cyclonon-2,3-ylene; 1,4-diaza-7-oxa-cyclonon-6,8-ylene; 1,4-diaza-7-oxa-cyclonon-2,2-ylidene; 1,4-dioxan-2,3-ylene; 1,4-dioxan-2,6-ylene; 1,4-dioxan-2,2-ylidene; tetrahydropyran-2,3-ylene; tetrahydropyran-2,6-ylene; tetrahydropyran-2,5-ylene; tetrahydropyran-2,2-ylidene; 1,4,7-trithia-cyclonon-2,3-ylene; 1,4,7-trithia-cyclonon-2,9-ylene; and 1,4,7-trithia-cyclonon-2,2-ylidene,

amine: the group $-N(R)_2$ wherein each R is independently selected from: hydrogen; C1-C6-alkyl; C1-C6-alkyl-C6H5; and phenyl, wherein when both R are C1-C6-alkyl both R together may form an -NC3 to an -NC5 heterocyclic ring with any remaining alkyl chain forming an alkyl substituent to the heterocyclic ring,

halogen: selected from the group consisting of: F; Cl; Br and I,

sulfonate: the group -$S(O)_2OR$, wherein R is selected from: hydrogen; C1-C6-alkyl; phenyl; C1-C6-alkyl-C6H5; Li; Na; K; Cs; Mg; and Ca.

sulfate: the group -$OS(O)_2OR$, wherein R is selected from: hydrogen; C1-C6-alkyl; phenyl; C1-C6-alkyl-C6H5; Li; Na; K; Cs; Mg; and Ca,

sulfone: the group -$S(O)_2R$, wherein R is selected from: hydrogen; C1-C6-alkyl; phenyl; C1-C6-alkyl-C6H5 and amine (to give sulfonamide) selected from the group: -NR'2, wherein each R' is independently selected from: hydrogen; C1-C6-alkyl; C1-C6-alkyl-C6H5; and phenyl, wherein when both R' are C1-C6-alkyl both R' together may form an -NC3 to an -NC5 heterocyclic ring with any remaining alkyl chain forming an alkyl substituent to the heterocyclic ring.

carboxylate derivative: the group –C(O)OR, wherein R is selected from: hydrogen; C1-C6-alkyl; phenyl; C1-C6-alkyl-C6H5; Li; Na; K; Cs; Mg; and Ca,

carbonyl derivative: the group -C(O)R, wherein R is selected from: hydrogen; C1-C6-alkyl; phenyl; C1-C6-alkyl-C6H5 and amine (to give amide) selected from the group: -NR'2, wherein each R' is independently selected from: hydrogen; C1-C6-alkyl; C1-C6-alkyl-C6H5; and phenyl, wherein when both R' are C1-C6-alkyl both R' together may form an -NC3 to an -NC5 heterocyclic ring with any remaining alkyl chain forming an alkyl substituent to the heterocyclic ring,

phosphonate: the group $–P(O)(OR)_2$, wherein each R is independently selected from: hydrogen; C1-C6-alkyl; phenyl; C1-C6-alkyl-C6H5; Li; Na; K; Cs; Mg; and Ca,

phosphate: the group $–OP(O)(OR)_2$, wherein each R is independently selected from: hydrogen; C1-C6-alkyl; phenyl; C1-C6-alkyl-C6H5; Li; Na; K; Cs; Mg; and Ca,

phosphine: the group -$P(R)_2$. wherein each R is independently selected from: hydrogen; C1-C6-alkyl; phenyl; and C1-C6-alkyl-C6H5.

phosphine oxide: the group -$P(O)R_2$, wherein R is independently selected from: hydrogen; C1-C6-alkyl; phenyl; and C1-C6-alkyl-C6H5; and amine (to give phosphonamidate) selected from the group: -NR'2, wherein each R' is independently selected from: hydrogen; C1-C6-alkyl; C1-C6-alkyl-C6H5; and phenyl. wherein when both R' are C1-C6-alkyl both R' together may form an -NC3 to an -NC5 heterocyclic ring with any remaining alkyl chain forming an alkyl substituent to the heterocyclic ring.

Unless otherwise specified the following are more preferred group restrictions that may be applied to groups found within compounds disclosed herein:

alkyl: linear and branched C1-C6-alkyl,

alkenyl: C3-C6-alkenyl,

cycloalkyl: C6-C8-cycloalkyl.

alkoxy: C1-C4-alkoxy,

alkylene: selected from the group consisting of: methylene; 1,2-ethylene; 1,3-propylene; butan-2-ol-1,4-diyl; 1,4-butylene; cyclohexane-1,1-diyl; cyclohexan-1,2-diyl; cyclohexan-1,4-diyl; cyclopentane-1,1-diyl; and cyclopentan-1,2-diyl.

aryl: selected from group consisting of: phenyl; biphenyl; naphthalenyl; anthracenyl; and phenanthrenyl,

arylene: selected from the group consisting of: 1,2-phenylene; 1,3-phenylene; 1,4-phenylene; 1,2-naphtalenylene; 1,4-naphtalenylene; 2,3-naphtalenylene and 1-hydroxy-2,6-phenylene,

heteroaryl: selected from the group consisting of: pyridinyl; pyrimidinyl; quinolinyl; pyrazolyl; triazolyl; isoquinolinyl; imidazolyl; and oxazolidinyl, wherein the heteroaryl may be connected to the compound via any atom in the ring of the selected heteroaryl.

heteroarylene: selected from the group consisting of: pyridin-2,3-diyl; pyridin-2,4-diyl; pyridin-2,6-diyl; pyridin-3,5-diyl; quinolin-2,3-diyl; quinolin-2,4-diyl; isoquinolin-1,3-diyl; isoquinolin-1,4-diyl; pyrazol-3,5-diyl; and imidazole-2,4-diyl.

heterocycloalkyl: selected from the group consisting of: pyrrolidinyl; morpholinyl; piperidinyl; piperidinyl; 1,4-piperazinyl; tetrahydrofuranyl; 1,4,7-triazacyclononanyl; 1,4,8,11-tetraazacyclotetradecanyl; 1,4,7,10,13-pentaazacyclopentadecanyl; 1,4,7,10-tetraazacyclododecanyl; and piperazinyl, wherein the heterocycloalkyl may be connected to the compound via any atom in the ring of the selected heterocycloalkyl.

heterocycloalkylene: selected from the group consisting of: piperidin-2,6-ylene; piperidin-4,4-ylidene; 1,4-piperazin-1,4-ylene; 1,4-piperazin-2,3-ylene; 1,4-piperazin-2,6-ylene; tetrahydrothiophen-2,5-ylene; tetrahydrothiophen-3,4-ylene; tetrahydrofuran-2,5-ylene; tetrahydrofuran-3,4-ylene; pyrrolidin-2,5-ylene; pyrrolidin-2,2-ylidene; 1,4,7-triazacyclonon-1,4-ylene; 1,4,7-triazacyclonon-2,3-ylene; 1,4,7-triazacyclonon-2,2-ylidene; 1,4,8,11-tetraazacyclotetradec-1,4-ylene; 1,4,8,11-tetraazacyclotetradec-1,8-ylene;
1,4,8,11-tetraazacyclotetradec-2,3-ylene; 1,4,8,11-tetraazacyclotetradec-2,2-ylidene; 1,4,7,10-tetraazacyclododec-1,4-ylene; 1,4,7,10-tetraazacyclododec-1,7-ylene; 1,4,7,10-tetraazacyclododec-2,3-ylene; 1,4,7,10-tetraazacyclododec-2,2-ylidene; 1,4,7,10,13-pentaazacyclopentadec-1,4-ylene; 1,4,7,10,13-pentaazacyclopentadec-1,7-ylene; 1,4-diaza-7-thia-cyclonon-1,4-ylene; 1,4-diaza-7-thia-cyclonon-2,3-ylene; 1,4-diaza-7-thia-cyclonon-2,2-ylidene; 1,4-diaza-7-oxa-cyclonon-1,4-ylene; 1,4-diaza-7-oxa-cyclonon-2,3-ylene;1,4-diaza-7-oxa-cyclonon-2,2-ylidene; 1,4-dioxan-2,6-ylene; 1,4-dioxan-2,2-ylidene; tetrahydropyran-2,6-ylene; tetrahydropyran-2,5-ylene; and tetrahydropyran-2,2-ylidene,

amine: the group -$N(R)_2$, wherein each R is independently selected from: hydrogen; C1-C6-alkyl; and benzyl,

halogen: selected from the group consisting of: F and Cl,

sulfonate: the group -$S(O)_2OR$, wherein R is selected from: hydrogen; C1-C6-alkyl; Na; K; Mg; and Ca,

sulfate: the group -$OS(O)_2OR$, wherein R is selected from: hydrogen; C1-C6-alkyl; Na; K; Mg; and Ca,

sulfone: the group -$S(O)_2R$, wherein R is selected from: hydrogen; C1-C6-alkyl; benzyl and amine selected from the group: -NR'2, wherein each R' is independently selected from: hydrogen; C1-C6-alkyl; and benzyl.

carboxylate derivative: the group –C(O)OR, wherein R is selected from hydrogen; Na; K; Mg; Ca; C1-C6-alkyl; and benzyl,

carbonyl derivative: the group: -C(O)R, wherein R is selected from: hydrogen; C1-C6-alkyl; benzyl and amine selected from the group: -NR'2, wherein each R' is independently selected from: hydrogen; C1-C6-alkyl; and benzyl,

phosphonate: the group –$P(O)(OR)_2$, wherein each R is independently selected from: hydrogen; C1-C6-alkyl; benzyl; Na; K; Mg; and Ca,

phosphate: the group –$OP(O)(OR)_2$, wherein each R is independently selected from: hydrogen; C1-C6-alkyl; benzyl; Na; K; Mg; and Ca,

phosphine: the group -$P(R)_2$, wherein each R is independently selected from: hydrogen; C1-C6-alkyl; and benzyl,

phosphine oxide: the group -$P(O)R_2$, wherein R is independently selected from: hydrogen; C1-C6-alkyl; benzyl and amine selected from the group: -NR'2, wherein each R' is independently selected from: hydrogen; C1-C6-alkyl; and benzyl.

The invention will now be further illustrated by way of the following non-limiting examples:

EXAMPLES

The following compounds were prepared and tested in Examples 1 and 2 for catalytic bleaching activity using air:

Compound 1: [Fe(N-methyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine)Cl](PF_6)

Compound 2: [Fe(N-trimethylammoniumpropyl-N,N',N'-tris(pyridin-2-ylmethyl)-ethylenediamine)Cl](PF_6)$_2$

Compound 3: [Fe(N-(2-hydroxyethylene)-N,N',N'-tris(pyridin-2-ylmethyl)-ethylenediamine)Cl]PF_6

Compound 4: [Fe(N,N,N',N'-tetrakis(3-methyl-pyridin-2-ylmethyl)-ethylene-diamine)](PF_6)$_2$

Compound 5: N,N'-dimethyl-N,N'-bis(pyridin-2-ylmethyl)-cyclohexane-1,2-diamine

Compound **6**: N,N'-dimethyl-N,N'-bis(pyridin-2-ylmethyl)-cyclohexane-1,2-diamine + $Co(ClO_4)_2.6H_2O$

Compound **7**: N,N'-dimethyl-N,N'-bis(pyridin-2-ylmethyl)-cyclohexane-1,2-diamine + $Fe(ClO_4)_2.\ 6H_2O$

Compound **8**: N,N'-dimethyl-N,N'-bis(pyridin-2-ylmethyl)-cyclohexane-1,2-diamine + $Mn(ClO_4)_2.\ 6H_2O$

Compound **9**: N-(2-hydroxyethylene)-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine

Compound **10**: N-(2-hydroxyethylene)-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine + $Co(ClO_4)_2.\ 6H_2O$

Compound **11**: N-(2-hydroxyethylene)-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine + $Fe(ClO_4)_2.\ 6H_2O$

Compound **12**: N-(2-hydroxyethylene)-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine +$Mn(ClO_4)_2.\ 6H_2O$

Compound **13**: N-(2-hydroxyethylene)-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine +$Cu(ClO_4)_2.6H_2O$

Compound **14**: N-methyl-N,N',N'-tris(pyridin-2-ylmethyl)-ethylenediamine

Compound **15**: N-methyl-N,N',N'-tris(pyridin-2-ylmethyl)-ethylenediamine + $Co(ClO_4)_2.\ 6H_2O$

Compound **16**: N-methyl-N,N',N'-tris(pyridin-2-ylmethyl)-ethylenediamine + $Fe(ClO_4)_2.\ 6H_2O$

Compound **17**: N-methyl-N,N',N'-tris(pyridin-2-ylmethyl)-ethylenediamine + $Mn(ClO_4)_2.\ 6H_2O$

Compound **18**: N-methyl-N,N',N'-tris(5-ethyl-pyridin-2-ylmethyl)-ethylenediamine

Compound **19**: N-methyl-N,N',N'-tris(5-ethyl-pyridin-2-ylmethyl)-ethylenediamine + $Co(ClO_4)_2.\ 6H_2O$

Compound **20**: N-methyl-N,N',N'-tris(5-ethyl-pyridin-2-ylmethyl)-ethylenediamine + $Fe(ClO_4)_2.\ 6H_2O$

Compound **21**: N-methyl-N,N',N'-tris(5-ethyl-pyridin-2-ylmethyl)-ethylenediamine + $Mn(ClO_4)_2$. $6H_2O$

Compound **22**: N-methyl-N,N',N'-tris(5-ethyl-pyridin-2-ylmethyl)-ethylenediamine + $Cu(ClO_4)_2$. $6H_2O$

Compound **23**: N-methyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)-ethylenediamine

Compound **24**: N-methyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)-ethylenediamine + $Co(ClO_4)_2$. $6H_2O$

Compound **25**: N-methyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)-ethylenediamine + $Fe(ClO_4)_2$. $6H_2O$

Compound **26**: N-methyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)-ethylenediamine + $Mn(ClO_4)_2$. $6H_2O$

Compound **27**: N-methyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)-ethylenediamine + $Cu(ClO_4)_2$. $6H_2O$

Compound **28**: N-methyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine

Compound **29**: N-methyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine + $Co(ClO_4)_2$. $6H_2O$

Compound **30**: N-methyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine + $Fe(ClO_4)_2$. $6H_2O$

Compound **31**: N-methyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine + $Mn(ClO_4)_2$. $6H_2O$

Compound **32**: N-methyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine + $Cu(ClO_4)_2$. $6H_2O$

Compound **33**: N-benzyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine

Compound **34**: N-benzyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine + $Co(ClO_4)_2$. $6H_2O$

Compound **35**: N-benzyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine + $Fe(ClO_4)_2$. $6H_2O$

Compound **36**: N-benzyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine + $Mn(ClO_4)_2$. $6H_2O$

Compound **37**: N-benzyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine + $Cu(ClO_4)_2$. $6H_2O$

Compound **38**: N-ethyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine

Compound **39**: N-ethyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine + $Co(ClO_4)_2$. $6H_2O$

Compound **40**: N-ethyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine + $Fe(ClO_4)_2$. $6H_2O$

Compound **41**: N-ethyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine + $Mn(ClO_4)_2$. $6H_2O$

Compound **42**: N-ethyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine + $Cu(ClO_4)_2$. $6H_2O$

Compound **43**: N,N,N'-tris(3-methyl-pyridin-2-ylmethyl)-N'(2'-methoxy-ethyl-1)-ethylenediamine

Compound **44**: N,N,N'-tris(3-methyl-pyridin-2-ylmethyl)-N'-(2'-methoxy-ethyl-1)-ethylenediamine + $Co(ClO_4)_2$. $6H_2O$

Compound **45**: N,N,N'-tris(3-methyl-pyridin-2-ylmethyl)-N'-(2'-methoxy-ethyl-1)-ethylenediamine + $Fe(ClO_4)_2$. $6H_2O$

Compound **46**: N,N,N'-tris(3-methyl-pyridin-2-ylmethyl)-N'-(2'-methoxy-ethyl-1)-ethylenediamine + $Mn(ClO_4)_2$. $6H_2O$

Compound **47**: N,N,N'-tris(3-methyl-pyridin-2-ylmethyl)-N'-(2'-methoxy-ethyl-1)-ethylenediamine + $Cu(ClO_4)_2$. $6H_2O$

Compound **48**: N,N,N'-tris(1-methyl-benzimidazol-2-yl)-N'-methyl-ethylenediamine

Compound **49**: N,N,N'-tris(1-methyl-benzimidazol-2-yl)-N'-methyl-ethylenediamine + $Co(ClO_4)_2$. $6H_2O$

Compound **50**: N,N,N'-tris(1-methyl-benzimidazol-2-yl)-N'-methyl-ethylenediamine + $Fe(ClO_4)_2$. $6H_2O$

Compound **51**: N,N,N'-tris(1-methyl-benzimidazol-2-yl)-N'-methyl-ethylenediamine + $Mn(ClO_4)_2$. $6H_2O$

Compound **52**: N,N,N'-tris(1-methyl-benzimidazol-2-yl)-N'-methyl-ethylenediamine + $Cu(ClO_4)_2$. $6H_2O$

Compound **53**: [Fe(N-(furan-2-yl)-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine)Cl](PF_6)

Compound **54**: N-(2-hydroxyethylene)-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)-ethylenediamine

Compound **55**: N-(2-hydroxyethylene)-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)-ethylenediamine + $Co(ClO_4)_2$. $6H_2O$

Compound **56**: N-(2-hydroxyethylene)-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)-ethylenediamine + $Fe(ClO_4)_2$. $6H_2O$

Compound **57**: N-(2-hydroxyethylene)-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)-ethylenediamine + $Mn(ClO_4)_2$. $6H_2O$

SYNTHESES OF LIGANDS AND COMPLEXES

Synthesis of starting materials for ligand synthesis:

Synthesis of *N*-benzyl amino acetonitrile. *N*-benzyl amine (5.35 g, 50 mmol) was dissolved in a water : methanol mixture (50 mL, 1:4). Hydrochloric acid (aq., 30 %) was added until the pH reached 7.0. Added was NaCN (2.45 g, 50 mmol). After cooling to 0 °C, formaline (aq. 35 %, 4.00 g, 50 mmol) was added. The reaction was followed by TLC (aluminium oxide; EtOAc : Et_3N = 9:1) until benzylamine could be detected. Subsequently the methanol was evaporated *in vacuo* and the remaining oil "dissolved" in water. The aqueous phase was extracted with methylene chloride (3 x 50 mL). The organic layers were collected and the solvent removed *in vacuo*. The residue was purified by Kugelrohr distillation (p = 20 mm Hg, T = 120 °C) giving *N*-benzyl amino acetonitrile (4.39 g, 30 mmol, 60 %) as a colourless oil.

^{1}H NMR: δ 7.37 - 7.30 (m. 5H), 3.94 (s. 2H). 3.57 (s. 2H). 1.67 (br s. 1H):

^{13}C NMR: δ 137.74, 128.58, 128.46. 128.37, 127.98. 127.62. 117.60. 52.24. 36.19.

Synthesis of *N*-ethyl amino acetonitrile. This synthesis was performed analogously to the synthesis reported for *N*-benzyl amino acetonitrile. However, detection was done by dipping the TLC plate in a solution of $KMnO_4$ and heating the plate until bright spots appeared. Starting from ethylamine (2.25 g, 50 mmol), pure *N*-ethyl amino acetonitrile (0.68 g, 8.1 mmol, 16 %) was obtained as a slightly yellow oil.

^{1}H NMR: δ 3.60 (s, 2H), 2.78 (q, J = 7.1, 2H), 1.22 (br s, 1H). 1.14 (t. J = 7.2, 3H):

^{13}C NMR: δ 117.78, 43.08, 37.01, 14.53.

Synthesis of *N*-ethyl ethylene-1,2-diamine. The synthesis was performed according to Hageman; J.Org.Chem.; 14; 1949; 616, 634, starting from *N*-ethyl amino acetonitrile.

Synthesis of *N*-benzyl ethylene-1,2-diamine. Sodium hydroxide (890 mg: 22.4 mmol) was dissolved in ethanol (96 %, 20 mL), the process taking the better part of 2 hours. Added was *N*-benzyl amino acetonitrile (4, 2.92 g, 20 mmol) and Raney Nickel (approx. 0.5 g). Hydrogen pressure was applied (p = 3.0 atm.) until hydrogen uptake ceased. The mixture was filtered over Cellite, washing the residue with ethanol. The filter should not run dry since Raney Nickel is relatively pyrophoric. The Cellite containing the Raney Nickel was destroyed by putting the mixture in dilute acid, causing gas formation). The ethanol was evaporated in *in vacuo* and the residue dissolved in water. Upon addition of base (aq. NaOH, 5N) the product oiled out and was extracted with chloroform (3 x 20 mL). After evaporation of the solvent *in vacuo* the ^{1}H NMR showed the presence of benzylamine. Separation was enforced by column chromatography (silica gel; MeOH : EtOAc : Et_3N = 1:8:1) yielding the benzyl amine, followed by the solvent mixture MeOH : EtOAc : Et_3N = 5:4:1. Detection was done by using aluminium oxide as a solid phase in TLC, yielding pure *N*-benzyl ethylene-1,2-diamine (2.04 g, 13.6 mmol, 69 %).

^{1}H NMR: δ 7.33 - 7.24 (m, 5H), 3.80 (s, 2H), 2.82 (t, J = 5.7, 2H), 2.69 (t, J = 5.7, 2H), 1.46 (br s, 3H); ^{13}C NMR: δ 140.37, 128.22, 127.93, 126.73, 53.73, 51.88, 41.66.

Synthesis of 2-acetoxymethyl-5-methyl pyridine. 2,5-Lutidine (31.0 g, 290 mmol), acetic acid (180 mL) and hydrogen peroxide (30 mL, 30 %) were heated at 70-80 °C for 3hours. Hydrogen peroxide (24 mL, 30 %) was added and the subsequent mixture heated for 16 hours at 60-70 °C. Most of the mixture of (probably) hydrogen peroxide, water, acetic acid, and peracetic acid was removed *in vacuo* (rotavap, water bath 50 °C until p = 20 mbar). The resulting mixture containing the *N*-oxide was added dropwise to acetic anhydride heated under reflux. This reaction was highly exothermic, and was controlled by the dropping speed. After heating under reflux for an hour, methanol was added dropwise. This reaction was highly exothermic. The resulting mixture was heated under reflux for another 30 minutes. After evaporation of the methanol (rotavap, 50 °C until p = 20 mbar), the resulting mixture was purified by Kugelrohr distillation (p = 20 mm Hg, T = 150 °C). The clear oil that was obtained still contained acetic acid. This was removed by extraction (CH_2Cl_2, $NaHCO_3$ (sat.)) yielding the pure acetate of 2-acetoxymethyl-5-methyl pyridine (34.35 g, 208 mmol, 72 %) as a slightly yellow oil.

^{1}H NMR: δ 8.43 (s, 1H), 7.52 (dd, J = 7.8, J = 1.7, 1H), 7.26 (d, J = 7.2, 1H), 5.18 (s, 2H), 2.34 (s, 3H), 2.15 (s, 3H);

^{13}C NMR: δ 170.09, 152.32, 149.39, 136.74, 131.98, 121.14, 66.31, 20.39, 17.66.

Synthesis of 2-acetoxymethyl-5-ethyl pyridine. This synthesis was performed analogously to the synthesis reported for 2-acetoxymethyl-5-methyl pyridine. Starting from 5-ethyl-2-methyl pyridine (35.10 g, 290 mmol), pure 2-acetoxymethyl-5-ethyl pyridine (46.19 g, 258 mmol, 89%) was obtained as a slightly yellow oil.

^{1}H NMR: δ 8.47 (s, 1H), 7.55 (d, J = 7.8, 1H), 7.29 (d, J = 8.1, 1H), 2.67 (q, J = 7.8, 2H), 2.14 (s, 3H), 1.26 (t, J = 7.77, 3H);

^{13}C NMR: δ 170.56, 152.80, 149.11, 138.47, 135.89, 121.67, 66.72, 25.65, 20.78, 15.13.

Synthesis of 2-acetoxymethyl-3-methyl pyridine. This synthesis was performed analogously to the synthesis reported for 2-acetoxymethyl-5-methyl pyridine. The only difference was the reversal of the Kugelrohr distillation and the extraction. According

to ^{1}H NMR a mixture of the acetate and the corresponding alcohol was obtained. Starting from 2,3-picoline (31.0 g, 290 mmol), pure 2-acetoxymethyl-3-methyl pyridine (46.19 g, 258 mmol, 89%, calculated for pure acetate) was obtained as a slightly yellow oil.

^{1}H NMR: δ 8.45 (d, J = 3.9, 1H), 7.50 (d, J = 8.4, 1H), 7.17 (dd, J = 7.8, J = 4.8, 1H), 5.24 (s, 2H), 2.37 (s, 3H), 2.14 (s, 3H).

Synthesis of 2-hydroxymethyl-5-methyl pyridine. 2-Acetoxymethyl-5-methyl pyridine (30 g, 182 mmol) was dissolved in hydrochloric acid (100 mL, 4 N). The mixture was heated under reflux, until TLC (silica gel; triethylamine:ethyl acetate:petroleum ether 40-60 = 1:9:19) showed complete absence of the acetate (normally 1 hour). The mixture was cooled, brought to pH > 11, extracted with dichloromethane (3 x 50 mL) and the solvent removed *in vacuo*. Pure 2-hydroxymethyl-5-methyl pyridine (18.80 g, 152 mmol, 84 %) was obtained by Kugelrohr distillation (p = 20 mm Hg, T = 130 °C) as a slightly yellow oil.

^{1}H NMR: δ 8.39 (s, 1H), 7.50 (dd, J = 7.8, J = 1.8, 1H), 7.15 (d, J = 8.1, 1H), 4.73 (s, 2H), 3.83 (br s, 1H), 2.34 (s, 3H);

^{13}C NMR: δ 156.67, 148.66, 137.32, 131.62, 120.24, 64.12, 17.98.

Synthesis of 2-hydroxymethyl-5-ethyl pyridine. This synthesis was performed analogously to the synthesis reported for 2-hydroxymethyl-5-methyl pyridine. Starting from 2-acetoxymethyl-5-ethyl pyridine (40 g, 223 mmol), pure 2-hydroxymethyl-5-ethyl pyridine (26.02 g, 189 mmol, 85 %) was obtained as a slightly yellow oil.

^{1}H NMR: δ 8.40 (d, J = 1.2, 1H), 7.52 (dd, J = 8.0, J = 2.0, 1H), 7.18 (d, J = 8.1, 1H), 4.74 (s, 2H), 3.93 (br s, 1H), 2.66 (q, J = 7.6, 2H), 1.26 (t, J = 7.5, 3H);

^{13}C NMR: δ 156.67, 148.00, 137.87, 136.13, 120.27, 64.07, 25.67, 15.28.

Synthesis of 2-hydroxymethyl-3-methyl pyridine. This synthesis was performed analogously to the synthesis reported for 2-hydroxymethyl-5-methyl pyridine. Starting from 2-acetoxymethyl-3-methyl pyridine (25g (recalculated for the mixture), 152

mmol), pure 2-hydroxymethyl-3-methyl pyridine (15.51 g, 126 mmol, 83 %) was obtained as a slightly yellow oil.

^{1}H NMR: δ 8.40 (d, J = 4.5 , 1H)). 7.47 (d, J = 7.2, 1H), 7.15 (dd, J = 7.5, J = 5.1, 1H), 4.85 (br s, 1H), 4.69 (s, 1H), 2.22 (s, 3H);

^{13}C NMR: δ 156.06, 144.97, 137.38, 129.53, 121.91, 61.38, 16.30.

N-methyl-N,N',N'-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine.

2-Hydroxymethyl-3-methyl pyridine (5.00 g, 40.7 mmol) was dissolved in dichloromethane (30 mL). Thionyl chloride (30 mL) was added dropwise under cooling (ice bath). The resulting mixture was stirred for 1 hour and the solvents removed *in vacuo* (rotavap, until p = 20 mm Hg, T = 50 °C). To the resultant mixture was added dichloromethane (25 mL). Subsequently NaOH (5 N, aq.) was added dropwise until the pH (aqua) ≥ 11. The reaction was quite vigorous in the beginning, since part of the thionyl chloride was still present. N-methyl ethylene-1,2-diamine (502 mg, 6.8 mmol) and additional NaOH (5 N, 10 mL) were added. The reaction mixture was stirred at room temperature for 45 hours. The mixture was poured into water (200 mL), and the pH checked (≥ 14, otherwise addition of NaOH (aq. 5N)). The reaction mixture was extracted with dichloromethane (3 or 4 x 50 mL, until no product could be detected by TLC). The combined organic phases were dried and the solvent removed *in vacuo*. Purification was enforced as described before, yielding N-methyl-N,N',N'-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine as a slightly yellow oil. Purification was enforced by column chromatography (aluminium oxide 90 (activity II-III according to Brockmann); triethylamine : ethyl acetate : petroleum ether 40-60 = 1:9:10) until the impurities were removed according to TLC (aluminium oxide, same eluent, Rf ≈ 0.9). The compound was eluted using ethylacetate : triethyl amine = 9:1. N-methyl-N,N',N'-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine (**L2**, 1.743 g, 4.30 mmol, 63 %) was obtained.

^{1}H NMR: δ 8.36 (d, J = 3.0, 3H), 7.40 - 7.37 (m, 3H), 7.11-7.06 (m, 3H), 3.76 (s, 4H), 3.48 (s, 2H), 2.76 - 2.71 (m, 2H), 2.53 - 2.48 (m, 2H), 2.30 (s, 3H), 2.12 (s, 6H), 2.05 (s, 3H);

^{13}C NMR: δ 156.82, 156.77, 145.83, 145.67, 137.61, 133.14, 132.72, 122.10, 121.88, 62.32, 59.73, 55.19, 51.87, 42.37, 18.22, 17.80.

Compound 1: *N*-methyl-*N*,*N*',*N*'-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine iron(II)chloride.PF_6

$FeCl_2.4H_2O$ (51.2 mg.257 µmol) was dissolved in MeOH : H_2O = 1:1 (2.5 mL). The solution was heated to 50 °C. Added was *N*-methyl-*N*,*N*',*N*'-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine (100 mg, 257 µmol) in MeOH : H_2O = 1:1 (2.0 mL). Subsequently $NaPF_6$ (86.4 mg, 514 µmol) in H_2O (2.5 mL) was added dropwise. Cooling to room temperature, filtration and drying *in vacuo* (p = 0.05 mm Hg, T = room temperature) yielded the desired complex (149 mg, 239 µmol, 93 %) as a yellow solid. ^1H NMR (CD_3CN, paramagnetic): δ 167.17, 142.18, 117.01, 113.34, 104.79, 98.62, 70.77, 67.04, 66.63, 58.86, 57.56, 54.49, 51.68, 48.56, 45.90, 27.99, 27.36, 22.89, 20.57, 14.79, 12.14, 8.41, 8.16, 7.18, 6.32, 5.78, 5.07, 4.29, 3.82, 3.43, 2.91, 2.05, 1.75, 1.58, 0.94, 0.53, -0.28, -1.25, -4.82, -18.97, -23.46.

Compound 2: *N*-(trismethylammoniumpropyl)-*N*,*N*',*N*'-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine iron(II)chloride.PF_6

1.5 g of N,N,N'-Tris(pyridin-2ylmethyl)ethylenediamine (4.5 mmol) + 1.14 g of 1-bromo-3-trimethylammoniumpropane (4.5 mmol) were placed into 100 ml of acetonitrile. 4.5 g of KF on celite were added and the reaction refluxed for 48 hrs. The solvent was then removed under vaccum, the brown oily residue was extracted with DCM to remove the unreacted trispicen then water. The aqueous phase was evaporated under vaccum, the yellow residue was taken up in acetonitrile, heated until a precipitate formed. The precipitate was filtered off, the solvent removed to give a yellow oil. Yield : 59%. NMR: 8.5 ppm (d, 2H) ; 8.45 ppm (d, 1H) ; 7.65 ppm (2 * t.d, 3H) ; 7.45 (d, 2H) ; 7.25 (1H, d) ; 7.15 (m, 3H) ; 3.8 (s, 4H) ; 3.65 (s, 2H) ; 3.5 (m, 2H) ; 3.3 (s, 9H) ; 2.7 (s, 4H) ; 2.6 (t, 2H) ; 1.8 (m, 2H).

In 507 mg of $[L3^+]Br^-$ (ligand, 1 mmol) in MeOH (5 ml), was added 162.21 mg of $FeCl_3$ (1 mmol) in 5 ml MeOH. The reaction was left to stir at r.t. for a while then 489 mg of

NH_4PF_6 (3 mmol) were added. The reaction was left to stir for a while then transfered to the freezer. The formed precipitate was filtered off. rinced with diethylether and dried in a dessicator.

Yield : 45%

ESMS : m/z = 669 (attributed to $[LFeClPF_6]+$) ; 262 (attributed to $[LFeCl]^{2+}$) : 543 (attributed to $[LFeClF]^{+}$) ; 433 (attributed to L^{+})

Compound 3: $[Cl_3Fe(\mu\text{-}O)Fe$(N-(2-hydroxyethylene)-N,N',N'-tris(pyridin-2-ylmethyl)-ethylenediamine)Cl]Cl

Picolyl chloride (2.1 g, 12.8 mmol) was dissolved in a 0.8 ml water and 3 ml 5N NaOH (15 mmol) was added. The resulting mixture was added to N-hydroxyethyl-diethylene amine (0.4 g, 3.85 mmol) followed by 4 ml 5N NaOH (20 mmol) and cetyltrimethylammonium bromide (20 mg) and dichloromethane (1 ml) and the mixture was stirred at 20 C. After 4 days the mixture was extracted with an ether/toluene mix and the ether/toluene layer was washed with saturated aqueous NaCl. The organic layer was evaporated giving 1.5 g of an orange oil being the crude poroduct which was not further purified. ^{1}H NMR: d 8.48 (dd, 2H), 8.43 (dd, 1H), 7.58 (dt, 2H), 7.48 (dt, 1H), 7.42 (d, 2H), 7.20 (d 1H), 7.10 - 7.00 (m, 3H), 3.78 (s, 4H), 3.72 (s, 2H), 3.55 (t, J = 5.1, 2H), 2,74 (m, 2H), 2.70-2.60 (m, 4H); ^{13}C NMR: d 159.6, 159.4, 149.0, 148.9, 136.4, 123.2, 123.0, 122.8, 122.2, 122.0, 60.5, 60.4, 59.6, 56.6, 52.4, 52.2.

Iron complex: [(HOEtTripen)Fe(μ-O)(FeCl3)].Cl

To 151 mg (0.40 mmol) of ligand was added a solution of 130 mg FeCl3 (anhydrous) in 10 ml abs.ethanol. An immediate precipitation of a yellow solid was observed. The solid was isolated by filtration, washed with ethanol, diethyl ether and dried over a nitrogen flow giving 233 mg of an amorphous yellow powder. Mass spectr. m/z: 610 [(HOEtTripen)Fe(μ-O)(FeCl3)]+, 468 [(HOEtTripen)FeCl)]+, 467 [(OEtTripen)FeCl)]+.

Compound 4: [Fe(N,N,N',N'-tetrakis(3-methyl-pyridin-2-ylmethyl)-ethylene-diamine)]$(ClO_4)_2$

3-Methyl-2-picolyl-chloride [Jeromin G.E., Orth W., Rapp B. &Weiss W.; Chem. Ber. **120**, 649 (1987)]

To a stirred solution of 21.4g 2,3-dimethyl-pyridine in 80ml chloroform was added at reflux temperature 26g trichloro-isocyanuric acid as a slurry in 80ml chloroform over 2h while refluxing and stirring. After completion of the addition the mix was allowed to reflux for another 2h and subsequently allowed to cool while stirring. The mixture was filtered to remove the formed isocyanuric acid. The chloroform layer was washed with 10ml 5% KOH/H_2O. The chloroform layer was again filtered and now washed with 10ml 3% HCl/H_2O to remove unreacted lutidine. The chloroform layer was clarified by filtration and now extracted with 50ml 15% hydrochloric acid. The aqueous layer was evaporated giving an oil in contrast to the authors of the reference who stated that a solid was formed. TLC (eluent 90% CH_2Cl_2 / 10 % MeOH cont. 7N NH_3) showed only one product to be present which was not the starting lutidin. The oil was used without further purification for following reaction steps.

To 12g of the residue obtained in the reaction above was added at 0°C 20ml of 5N NaOH. The mixture turned red brown and cloudy. Now 0.5ml ethylene diamine was added at 0°C while stirring and the mix was allowed to warm to 25°C and stirred for 16h. TLC analysis showed the product formed to dissolved well in dichloromethane but not very well in diethyl ether. Therefore first 0ml ether was added and stirred for 5' and subsequently decanted. This procedure was repeated three times. A solid fraction formed on top of the aqueous phase remained in the aqueous phase. Subsequently the aqueous phase was extracted with dichloromethane three times. The combined dichloromethane layers were dried over sodium sulfate, filtered and evaporated giving 2.7g of a dark red powder.

^1H NMR ($CDCl_3$) δ (ppm): 2.03 (s, 12H, 4xCH_3), 2.58 (s, 4H, -CH_2CH_2-), 3.62 (s, 8H, Py-CH_2-N), 7.01 (m, 4H, Py-H), 7.34 (m, 4H, Py-H), 8.27 (m, 4H, Py-H)

^{13}C NMR ($CDCl_3$) δ (ppm): 18.0, 52.3, 60.0, 122.3, 133.4, 137.8, 145.8, 157.0

[Fe(3Me$_4$-tpen)](ClO$_4$)$_2$

To 0.5g of $3Me_4$-tpen in 1 ml acetonitrile was added 0.35g of iron(II) perchlorate hexahydrate followed by 0.25g sodium perchlorate in 1ml methanol. Over 16h ethyl acetate was allowed to diffuse into the mixture giving a precipitate. This was isolated by filtration washed with ethyl acetate and dried in vacuo at 50°C giving 0.37g of an orange brown powder. The UV/Vis spectrum is also temperature dependent. At 25°C (CH_3CN) λ_{max} (ε mol/lcm.): 420 nm (10500). 258 nm (17200). ESP Mass spectr. m/z: 268.2 [Fe+3Me4-tpen]

Compound 5: N,N'-dimethyl-N,N'-bis(pyridin-2-ylmethyl)-cyclohexane-1,2-diamine

N,N'-dimethyl-N,N'-bis(pyridin-2-ylmethyl)-cyclohexane-1,2-diamine was synthesised as described elsewhere: C. Li, et al, J. Chem. Soc., Dalton Trans. (1991). 1909-14

Compound 9: *N*-hydroxyethyl-*N*,*N*',*N*'-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine

This synthesis is performed analogously to the synthesis for **L**. Starting from 2-hydroxymethyl-3-methyl pyridine (3.49 g, 28.4 mmol), and *N*-hydroxyethyl ethylene-1,2-diamine (656 mg 6.30 mmol), after 7 days *N*-hydroxyethyl-*N*,*N*',*N*'-tris(3-methylpyridin-2-ylmethyl)ethylene-1,2-diamine (379 mg, 0.97 mmol, 14 %) was obtained.

^{1}H NMR: δ 8.31 - 8.28 (m, 3H), 7.35 - 7.33 (m, 3H), 7.06 - 7.00 (m, 3H), 4.71 (br s, 1H), 3.73 (s, 4H), 3.61 (s, 2H), 3.44 (t, J = 5.1, 2H), 2.68 (s, 4H), 2.57 (t, J = 5.0, 2H), 2.19 (s, 3H), 2.10 (s, 6H); ^{13}C NMR: δ 157.01, 156.88, 145.91, 145.80, 137.90, 137.83, 133.30, 131.89, 122.30, 121.97, 59.60, 59.39, 57.95, 56.67, 51.95, 51.22, 18.14, 17.95.

Compound 14: N-methyl-N,N',N'-tris(pyridin-2-ylmethyl)-ethylenediamine

The ligand compound **14** was prepared according to Bernal, Ivan; Jensen, Inge Margrethe; Jensen, Kenneth B.; McKenzie, Christine J.; Toftlund, Hans; Tuchagues, Jean-Pierre; J.Chem.Soc.Dalton Trans.; 22; 1995; 3667-3676.

Compound 18: N-methyl-N,N',N'-tris(5-ethyl-pyridin-2-ylmethyl)-ethylenediamine

This ligand compound **18** was synthesised analogously to the synthesis for **L6**. Starting from 2-hydroxymethyl-5-ethyl pyridine (3.00 g, 21.9 mmol), and *N*-methyl ethylene-1,2-diamine (360 mg, 4.86 mmol), after 7 days *N*-methyl-*N*,*N*',*N*'-tris(5-ethylpyridin-2-ylmethyl)ethylene-1,2-diamine (**L7**, 545 mg, 1.26 mmol, 26 %) was obtained.

^{1}H NMR: δ 8.34 (s, 3H), 7.44 - 7.39 (m, 5H), 7.26 (d, *J* = 6.6, 1H), 3.80 (s, 4H), 3.59 (s, 2H), 2.77 - 2.72 (m, 2H), 2.66 - 2.57 (m, 8H), 2.18 (s, 3H), 1.23 (t, *J* = 7.5, 9H);

^{13}C NMR: δ 157.14, 156.70, 148.60, 148.53, 137.25, 135.70, 122.59, 122.43, 63.91, 60.48, 55.65, 52.11, 42.82, 25.73, 15.36.

Compound 23: N-methyl-N,N',N'-tris(5-methyl-pyridin-2-ylmethyl)-ethylenediamine

2-hydroxymethyl-5-methyl pyridine (2.70 g, 21.9 mmol) was dissolved in dichloromethane (25 mL). Thionyl chloride (25 mL) was added dropwise under cooling (ice bath). The resulting mixture was stirred for 1 hour and the solvents removed *in vacuo* (rotavap, until p = 20 mm Hg, T ± 35°C). The remaining oil was used directly in the synthesis of the ligands, since it was known from the literature that the free picolyl chlorides are somewhat unstable and are highly lachrymatory. To the resultant mixture was added dichloromethane (25 mL) and *N*-methyl ethylene-1,2-diamine (360 mg, 4.86 mmol). Subsequently NaOH (5 N, aq.) was added dropwise. The reaction was quite vigorous in the beginning, since part of the thionyl chloride was still present. The aqueous layer was brought to pH = 10, and additional NaOH (5 N, 4.38 mL) was added. The reaction mixture was stirred until a sample indicated complete conversion (7 days). The reaction mixture was extracted with dichloromethane (3 x 25 mL). The combined organic phases were dried and the solvent removed *in vacuo*. Purification was enforced by column chromatography (aluminium oxide 90 (activity II-III according to Brockmann); triethylamine : ethyl acetate : petroleum ether 40-60 = 1:9:10) until the impurities were removed according to TLC (aluminium oxide, same eluent, Rf ≈ 0.9). The compound was eluted using ethyl acetate : triethyl amine = 9:1, yielding *N*-methyl-*N*,*N*',*N*'-tris(5-methylpyridin-2-ylmethyl)ethylene-1,2-diamine (**L6**, 685 mg, 1.76 mmol, 36 %) as a slightly yellow oil.

^{1}H NMR: δ 8.31 (s, 3H) 7.43 - 7.35 (m, 5H), 7.21 (d, J = 7.8, 1H), 3.76 (s, 4H), 3.56 (s, 2H), 2.74 - 2.69 (m, 2H), 2.63 - 2.58 (m, 2H), 2.27 (s, 6H), 2.16 (s, 3H); ^{13}C NMR: δ 156.83, 156.43, 149.23, 149.18, 136.85, 136.81, 131.02, 122.41, 122.30, 63.83, 60.38, 55.53, 52.00, 42.76, 18.03.

Compound 33: N-benzyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine

The synthesis is performed analogously to the synthesis for L. Starting from 2-hydroxymethyl-3-methylpyridine (3.00 g 24.4 mmol), and *N*-benzyl ethylene-1,2-diamine (610 mg, 4.07 mmol), the ligand (1.363 g, 2.93 mmol, 72 %) was obtained. Column chromatography (aluminium oxide; Et_3N : EtOAc : petroleum ether 40-60 = 1:9:10). ^{1}H NMR: δ 8.33 - 8.29 (m, 3H), 7.37 - 7.33 (m, 3H), 7.21 - 7.03 (m, 8H), 3.66 (s, 4H), 3.60 (s, 2H), 3.42 (s, 2H), 2.72 - 2.67 (m, 2H), 2.50 - 2.45 (m, 2H), 2.23 (s, 3H), 2.03 (s, 6H); ^{13}C NMR: δ 157.17, 156.96, 145.83, 145.78, 139.29, 137.91, 137.80, 133.45, 133.30, 128.98, 127.85, 126.62, 122.28, 122.22, 59.99, 58.83, 51.92, 51.54, 18.40, 17.95.

Compound 38: N-ethyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine

N-ethyl-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine was synthesised analogously to the synthesis for L. Starting from 2-hydroxymethyl-3-methyl pyridine (25.00 g, 203 mmol) and *N*-ethyl ethylene-1,2-diamine (2.99 g, 34.0 mmol), the ligand (11.49 g, 28.5 mmol, 84 %) was obtained. Column chromatography (aluminium oxide; Et_3N : EtOAc : petroleum ether 40-60 = 1:9:30, followed by Et_3N : EtOAc = 1:9). ^{1}H NMR: δ 8.34 - 8.30 (m, 3H), 7.40 - 7.34 (m, 3H), 7.09 - 7.03 (m, 3H), 3.71 (s, 4H), 3.58 (s, 2H), 2.64 - 2.59 (m, 2H), 2.52 - 2.47 (m, 2H), 2.43 - 2.36 (m, 2H), 2.31 (s, 3H), 2.10 (s, 6H), 0.87 (t, J = 7.2, 3H); ^{13}C NMR: δ 157.35, 156.92, 145.65, 137.61, 133.14, 132.97, 122.09, 121.85, 59.81, 59.28, 51.98, 50.75, 48.02, 18.27, 17.80, 11.36.

Compound 43: N,N,N'-tris(3-methyl-pyridin-2-ylmethyl)-N'(2'-methoxy-ethyl-1)-ethylenediamine

Synthesis of N-methoxyethyl amino acetonitrile.

N-methoxyethylamine (3.75 g, 50 mmol) was dissolved in a water/methanol mixture (50 mL, 1 : 4). Hydrochloric acid (aq., 30 %) was added until the pH reached 7.0. Added was NaCN (2.45 g, 50 mmol). After cooling to 0 °C formaline (aq. 35 %, 4.00 g, 50 mmol) was added. The reaction was followed by TLC (aluminium oxide: EtOAc : Et_3N = 9 : 1) until benzylamine could be detected. Subsequently the methanol was evaporated *in vacuo* and the remaining oil "dissolved" in water. The aqueous phase was extracted with methylene chloride (3 x 50 mL). The organic layers were collected and the solvent removed *in vacuo*. The residue was purified by Kugelrohr distillation (p = 20 mm Hg, T = 120 °C) giving pure product (4.15 g, 36 mmol, 73 %) obtained as a slightly yellow oil. ^{1}H NMR: d 3.60 (s, 2H), 3.49 (t, J = 5.0, 2H), 3.33 (s, 3H), 2.87 (t, J = 5.0, 2 H), 1.76 (br s, 1H); ^{13}C NMR: d 117.69, 71.24, 58.63, 47.94, 42.68, 37.24.

Synthesis of N-methoxyethyl ethylene diamine

Sodium hydroxide (890 mg; 22.4 mmol) is dissolved in ethanol (96 %, 20 mL), the process taking the better part of 2 h. Added is *N*-methoxyethyl amino acetonitrile (2.28 g, 20 mmol) and Raney Nickel (approx. 0.5 g). Hydrogen pressure is applied (p = 3.0 atm.) until hydrogen uptake ceases. The mixture is filtered over Cellite and washing the residue with ethanol (CAUTION: The filter should not run dry since Raney Nickel is relatively pyroforic. The Cellite containing the Raney Nickel was destroyed by putting the mixture in dilute acid, causing gas formation). The ethanol is evaporated *in vacuo* and the residue dissolved in water. Upon addition of base (aq. NaOH, 5 N) the product oils out and is extracted with chloroform (3 x 20 mL). After evaporation of the solvent *in vacuo* the ^{1}H NMR showed the presence of the product. Column chromatography (aluminium oxide; CH_2Cl_2 : MeOH : Et_3N = 35 : 4 : 1, followed by CH_2Cl_2 : MeOH : Et_3N = 6 : 1 : 3). Starting from *N*-methoxyethyl amino acetonitrile (2.28 g, 20 mmol) pure **1e** (0.91 g, 7.71 mmol, 38 %) was obtained as a slightly yellow oil. ^{1}H NMR: d 3.49 (t, J = 5.1, 2H), 3.35 (s, 3H), 2.82 - 2.76 (m, 4H), 2.68 (t, J = 5.7, 2H), 1.70 (br s, 3H); ^{13}C NMR: d 71.74, 58.52, 52.19, 48.87, 41.41.

Synthesis of N-methoxyethyl-N,N',N'-tris(3-methylpyridinylmethyl)-1,2-ethylene diamine.

This synthesis is performed analogously to the synthesis for compound 4. Starting from 3-methyl-2-picolyl chloride (excess) and *N*-methoxyethyl-1,2-ethylene diamine (393 mg, 3.33 mmol) *N*-methoxyethyl-*N,N',N'*-tris(3-methylpyridinylmethyl)-1,2-ethylene diamine (1.023 g, 2.36 mmol, 71 %) was obtained. Column chromatography (aluminium oxide; Et_3N : EtOAc : Pet ether 40-60 = 1 : 9 : 10). ^1H NMR: d 8.33 - 8.28 (m, 3H), 7.36 - 7.34 (m, 3H), 7.06 - 7.02 (m, 3H), 3.70 (s, 4H), 3.66 (s, 2H), 3.26 (t, J = 6.2, 2H), 2.20 (s, 3H), 2.63 - 2.54 (m, 6H), 2.30 (s, 3H), 2.09 (s, 6H); ^{13}C NMR: d 157.22, 156.98, 145.75, 137.77, 137.74, 133.27, 133.17, 122.22, 122.06, 71.05, 60.41, 59.86, 58.42, 53.62, 52.13, 52.01, 18.27, 17.90.

Compound 48: N,N,N'-tris(1-methyl-benzimidazol-2-yl)-N'-methyl-1,2-ethylene diamine

Glycolic acid (5.2g, 75 mmol) and N-methyl-1,2-diaminobenzene (**10b**, 5.4 g, 50 mmol) were dissolved in aqueous HCl (4 N, 50 mL). This mixture was heated under reflux for 40 min. After cooling in a water bath the solution was filtered, and the filtrate basified with ammonia until no further precipitation could be observed. Filtration and drying *in vacuo* (p = 0.05 mm Hg, T = r.t.) gave pure **11** (5.31 g, 36 mmol, 78 %) as a white solid. ^1H NMR: d 7.67 - 7.63 (m, 1H), 7.26 - 7.21 (m, 3H), 4.86 (s, 2H), 4.74 (br s, 1H), 3.79 (s, 3H); ^{13}C NMR: d 153.82, 141.28, 135.70, 122.88, 122.22, 119.08, 109.32, 56.69, 29.84.

Synthesis of N-methyl-N,N',N'-tris(N-methylbenzimidazole-2-methyl)-1,2-ethylene diamine.

2-Hydroxymethyl-*N*-methyl benzimidazole (3.00 g, 18.5 mmol) was added in portions to thionyl chloride (50 mL). A clear purple solution was obtained that was heated under reflux for 1 h. The thionyl chloride was evaporated *in vacuo* (rotavap, until p = 20 mm Hg, T = 50 °C). To the resultant mixture was added dichloromethane (25 mL). Subsequently NaOH (5 N, aq.) was added dropwise until the pH (aqua) ≥ 11 (CAUTION! The reaction is quite vigorous in the beginning, since part of the thionyl chloride is still there). *N*-methyl-1,2-ethylene diamine (228 mg, 3.08 mmol) and additional NaOH (5 N, 10 mL) is added. The reaction is allowed to stir at room

temperature for 45 h. The mixture was poured into water (200 mL), and the pH checked (≥ 14, otherwise addition of NaOH (aq. 5N). The reaction mixture was extracted with dichloromethane (3 or 4 x 50 mL, until no product could be detected by TLC). The combined organic phases were dried and the solvent removed in *vacuo*. Purification was enforced by column chromatography (aluminium oxide 90 (activity II-III according to Brockmann); triethylamine : ethyl acetate = 1 : 9 yielding *N*-methyl-*N*,*N*',*N*'-tris(*N*-methylbenzimidazole-2-methyl)-1,2-ethylene diamine (987 mg, 1.95 mmol, 63 %) as a white solid. ^{1}H NMR: d 7.73 - 7.69 (m, 3H), 7.27 - 7.19 (m, 12H), 3.97 (s, 4H), 3.71 (s, 2H), 3.61 (s, 3H), 3.48 (s, 6H), 2.88 (t, J = 6.6, 2H), 2.63 (t, J = 6.8, 2H), 2.21 (s, 3H); ^{13}C NMR: d 151.54, 151.15, 142.13, 135.96, 122.72, 122.56, 122.06, 121.91, 119.60, 119.47, 109.18, 109.11, 55.09, 54.77, 52.32, 51.38, 42.92, 29.87, 29.55.

Compound 53: [Fe(N-(furan-2-yl)-N,N',N'-tris(3-methyl-pyridin-2-ylmethyl)-ethylenediamine)Cl](PF$_6$)

Synthesis N-(furan-2-ylmethyl)-ethane-1,2-diamine

Furan-2-carbaldehyde (1.92 g, 20 mmol) and ethylene diamine (3.6 g, 60 mmol) were dissolved in methanol (50 mL). The mixture was stirred for 30 minutes and subsequently $Na_2B_4O_7$. 10 H_2O (4.0 g, 10.5 mmol) and $NaBH_4$ (2.0 g, 53 mmol) were added. The resulting mixture was stirred for another 30 minutes. The reaction mixture was acidified by adding 6 N HCl. The resulting mixture was extracted with dichloromethane (1 x 50 mL). The aqueous phase was treated with sodium hydroxide solution (5 N) until the pH > 11. The aqueous phase was extracted with dichloromethane (3 x 50 mL). The combined organic layers from the basic extraction were dried by evaporation *in vacuo* and stripping with dichloromethane. Final purification was enforced by distillation (p = 20 mm Hg, T = 150 °C), yielding 1.65 g (13.3 mmol, 58 %) pure product.

^{1}H NMR (300 MHz, $CDCl_3$): d 7.35 (d, J = 1.5, 1H), 6.30 (dd, J = 3.2, J = 2.3, 1H), 6.17 (d, J = 3.3, 1H), 3.70 (s, 2H), 2.82 – 2.78 (m, 2H), 2.72 –2.65 (m, 2H), 1.53 (br s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$): d 153.97, 141.72, 110.05, 106.76, 51.64, 46.06, 41.62.

Synthesis N-(furan-2-ylmethylene)-N, N',N'-tris(3-methylpyridin-2-yl)-ethane-1,2-diamine.

(3-Methyl-pyridin-2-yl)-methanol (4.11 g, 30 mmol) was dissolved in dichloromethane (25 mL) and cooled to 0 °C. Thionylchloride (25 mL) was added dropwise. The resulting mixture was stirred for 1 h. Subsequently the thionylchloride was removed *in vacuo*. Dichloromethane (25 mL) was added and sodiumhydroxide solution (5 N) was added until the pH of the aqueous phase was > 11. Added was N-(furan-2-ylmethyl)-ethane-1,2-diamine (700 mg, 5.0 mmol). The reaction was stirred for 3 days. The pH of the aqueous phase was adjusted to >11 by the addition of sodium hydroxide solution (5 N). The aqueous phase was extracted with dichloromethane (3 x 50 mL). The combined organic phases were evaporated *in vacuo* and subsequently stripped with dichloromethane. Final purification was enforced by column chromatography (Alox, activity 2-3 according to Brockman; triethylamine : ethyl acetate, petroleum ether 40/60 = 1 : 9 : 10) yielding pure product (976 mg, 43 %) as a slightly yellow solid.
^{1}H NMR (300 MHz, $CDCl_3$): d 8.33 – 8.30 (m, 3H), 7.37 – 7.33 (m, 3H), 7.29 –7.28 (m, 1H), 7.08 - 7.03 (m, 3H), 6.24 – 6.22 (m, 1H), 6.01 (d, J = 3.3, 1H), 3.69 (s, 4H), 3.63 (s, 2H), 3.51 (s, 2H), 2.69 – 2.64 (m, 2H), 2.55 –2.51 (m, 2H), 2.23 (s, 3H), 2.06 (s, 6H); ^{13}C NMR (300 MHz, $CDCl_3$): d 157.08, 152.56, 145.85, 141.57, 137.85, 137.79, 133.35, 122.25, 122.12, 109.90, 108.48, 59.88, 59.32, 52.00, 51.03, 50.25, 18.24, 17.96.

The corresponding iron compound **53** was synthesised as described for compound **1**.

Compound 54: N-(2-hydroxyethylene)-N,N',N'-tris(3-ethyl-pyridin-2-ylmethyl)-ethylenediamine

Synthesis of 2-acetoxymethyl-5-ethyl pyridine.

5-ethyl-2-methyl pyridine (35.10 g, 290 mmol), acetic acid (180 mL) and hydrogen peroxide (30 mL, 30 %) were heated at 70-80 °C for 3 h. Hydrogen peroxide (24 mL, 30 %) was added and the subsequent mixture heated for 16 h. at 60-70 °C. Most of the mixture of (probably) hydrogen peroxide, water, acetic acid, and peracetic acid was

removed *in vacuo* (rotavap, water bath 50 °C until p = 20 mbar). The resulting mixture containing the *N*-oxide was added dropwise to acetic anhydride heated under reflux (CAUTION: this reaction is highly exothermic, and is controlled by the dropping speed). After heating under reflux for an hour, methanol is added dropwise (CAUTION: this reaction is highly exothermic), and the resulting mixture is heated under reflux for another 30 min. After evaporation of the methanol (rotavap, 50 °C until p = 20 mbar), the resulting mixture was purified by Kugelrohr distillation (p = 20 mm Hg, T = 150 °C). The clear oil that is obtained still contains acetic acid. This is removed by extraction (CH_2Cl_2, $NaHCO_3$ (sat.)) yielding the pure acetate (46.19 g, 258 mmol, 89 %) obtained as a slightly yellow oil. ^{1}H NMR: 8.47 (s, 1H), 7.55 (d, J = 7.8, 1H), 7.29 (d, J = 8.1, 1H), 2.67 (q, J = 7.8, 2H), 2.14 (s, 3H), 1.26 (t, J = 7.7, 3H); ^{13}C NMR: 170.56, 152.80, 149.11, 138.47, 135.89, 121.67, 66.72, 25.65, 20.78, 15.13.

Synthesis of 2-hydroxymethyl-5-ethyl pyridine

2-acetoxymethyl-5-ethyl pyridine (40 g, 223 mmol) was dissolved in hydrochloric acid (100 mL, 4 N). The mixture was heated under reflux, until TLC (silica gel; triethylamine/ethyl acetate/pet. ether 40-60 = 1/9/19) showed complete absence of the acetate (normally 1 h.). The mixture was cooled, brought to pH > 11, extracted with dichloromethane (3 x 50 mL) and the solvent removed *in vacuo* giving pure product (26.02 g, 189 mmol, 85 as a slightly yellow oil. ^{1}H NMR:8.40 (d, J = 1.2, 1H), 7.52 (dd, J = 8.0, J = 2.0, 1H), 7.18 (d, J = 8.1, 1H), 4.74 (s, 2H), 3.93 (br s, 1H), 2.66 (q, J = 7.6, 2H), 1.26 (t, J = 7.5, 3H); ^{13}C NMR: 156.67, 148.00, 137.87, 136.13, 120.27, 64.07, 25.67, 15.28.

Synthesis of N-methyl-N,N',N'-tris(5-ethylpyridinylmethyl)-1,2-ethylene diamine

5-ethyl-2-hydroxymethylpyridine (3.00 g, 21.9 mmol), was dissolved in dichloromethane (25 mL). Thionyl chloride (25 mL) was added dropwise under cooling (ice bath). The resulting mixture was stirred for 1 h. and the solvents removed *in vacuo* (rotavap, until p = 20 mm Hg, T = ± 35 °C). The remaining oil was used directly in the synthesis of the ligands, since it is known from literature that the free picolyl chlorides are somewhat unstable and are highly lachrymatory. To the resultant mixture was added dichloromethane (25 mL) and *N*-methyl-1,2-ethylene diamine (**1a**, 360 mg, 4.86 mmol).

Subsequently NaOH (5 N, aq.) was added dropwise. The aqueous layer is brought to pH = 10, and additional NaOH (5 N, 4.38 mL) is added. The reaction is allowed to stir until a sample indicated complete conversion (7 d.). The reaction mixture was extracted with dichloromethane (3 x 25 mL). The combined organic phases were dried and the solvent removed in *vacuo*. Purification was enforced by column chromatography (aluminium oxide 90 (activity II-III according to Brockmann); triethylamine/ethyl acetate/pet. ether 40-60 : 1/9/10) until the impurities were removed according to TLC (aluminium oxide, same eluent, Rf ≈ 0.9). The compound was eluted using ethyl acetate/triethyl amine : 9/1 yielding *N*-methyl-*N*,*N*',*N*'-tris(5-ethylpyridinylmethyl)-1,2-ethylene diamine (545 mg, 1.26 mmol, 26 %) was obtained. ^{1}H NMR: d 8.34 (s, 3H), 7.44 - 7.39 (m, 5H). 7.26 (d, *J* = 6.6, 1H), 3.80 (s, 4H), 3.59 (s, 2H), 2.77 - 2.72 (m, 2H), 2.66 - 2.57 (m, 8H), 2.18 (s, 3H), 1.23 (t, *J* = 7.5, 9H); ^{13}C NMR: d 157.14, 156.70, 148.60, 148.53, 137.25, 135.70, 122.59, 122.43, 63.91, 60.48, 55.65, 52.11, 42.82, 25.73, 15.36.

Experimental:

Example 1:

In an aqueous solution containing 10 mM carbonate buffer (pH 10) without and with 0.6 g/l LAS (linear alkylbenzene sulfonate) or containing 10 mM borate buffer (pH 8) without and with 0.6 g/l NaLAS, tomato-soya oil stained cloths were added and kept in contact with the solution under agitation for 30 minutes at 30 °C. In comparative experiments, the same experiments were done by addition of 10 μM of complex (compounds **1-4** and **53**, or 10 μM of transition-metal salt in combination with 20 μM ligand (compounds **5-52** and **54-57**) referred to in the table below.

After the wash, the cloths were rinsed with water and subsequently dried at 30 °C and the change in colour was measured immediately after drying with a Linotype-Hell scanner (ex Linotype). The change in colour (including bleaching) is expressed as the ΔE value. The measured colour difference (ΔE) between the washed cloth and the unwashed cloth is defined as follows:

$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$$

wherein ΔL is a measure for the difference in darkness between the washed and unwashed test cloth; Δa and Δb are measures for the difference in redness and yellowness respectively between both cloths. With regard to this colour measurement technique, reference is made to Commission International de l'Eclairage (CIE); Recommendation on Uniform Colour Spaces, colour difference equations, psychometric colour terms, supplement no 2 to CIE Publication, no 15, Colormetry, Bureau Central de la CIE, Paris 1978.

A higher ΔE value indicates a cleaner (whiter) cloth. Values of more than 5 ΔE units are clearly perceived, with values of more than 15 ΔE units being perceived as very nearly clean.

The results are shown below in Table 1:

Table 1

	pH 8 – LAS	pH 8 + LAS	pH 10 – LAS	pH 10 + LAS
TAED/H_2O_2	1	2	1	3
Blank	1	3	1	3
Compound 1	12	17	10	15
Compound 2	6	15	1	10
Compound 3	2	15	1	6
Compound 4	2	17	3	17
Compound 5	2	4	2	5
Compound 6	2	12	5	13
Compound 7	2	9	6	13
Compound 8	2	12	15	13
Compound 9	3	16	8	18
Compound 10	4	14	6	16
Compound 11	10	19	10	18
Compound 12	4	13	4	5
Compound 13	3	13	4	9
Compound 14	3	12	3	12
Compound 15	3	6	3	6
Compound 16	4	12	4	12
Compound 17	2	10	2	5
Compound 18	13	17	15	18
Compound 19	13	11	13	14
Compound 20	17	17	17	17
Compound 21	15	16	6	6
Compound 22	11	10	8	9
Compound 23	4	15	10	16
Compound 24	7	14	11	16
Compound 25	13	18	16	17
Compound 26	6	15	6	11
Compound 27	7	13	10	15
Compound 28	3	15	14	16
Compound 29	6	14	13	14

Compound 30	13	17	16	16
Compound 31	5	14	6	7
Compound 32	6	13	11	14
Compound 33	9	14	15	16
Compound 34	14	14	14	13
Compound 35	16	16	15	15
Compound 36	9	11	7	8
Compound 37	13	14	12	12
Compound 38	3	13	12	15
Compound 39	6	14	12	14
Compound 40	10	17	16	17
Compound 41	4	13	7	14
Compound 42	4	13	11	13
Compound 43	3	15	13	15
Compound 44	6	16	12	13
Compound 45	11	18	16	17
Compound 46	4	13	6	9
Compound 47	5	14	11	14
Compound 48	6	4	6	7
Compound 49	8	8	11	9
Compound 50	16	10	13	14
Compound 51	10	9	6	10
Compound 52	12	8	10	11
Compound 53	10	16	8	11
Compound 54	12	17	16	18
Compound 55	8	5	7	10
Compound 56	17	18	17	19
Compound 57	12	14	2	5

Example 2:

Bleach values expressed in ΔE, as defined above. Stain: curry oil stain. Washed for 30 min at 30 °C, rinsed, dried and measured. In all cases 10 μM of metal complex is added to the wash liquor (except for blank). The results are shown below in Table 2:

Table 2

	pH 8 + LAS	pH 10 + LAS
TAED/H_2O_2	9	21
Blank	4	15
Compound 1	22	27
Compound 2	16	25
Compound 3	20	27
Compound 53	15	27

CLAIMS:

1. A bleaching composition comprising, in an aqueous medium, atmospheric oxygen and a ligand which forms a complex with a transition metal, the complex catalysing bleaching of a substrate by the atmospheric oxygen, wherein the aqueous medium is substantially devoid of peroxygen bleach or a peroxy-based or -generating bleach system,

wherein the ligand forms a complex of the general formula (A1):

$$[M_aL_kX_n]Y_m \qquad (A1)$$

in which:

M represents a metal selected from Mn(II)-(III)-(IV)-(V), Cu(I)-(II)-(III), Fe(II)-(III)-(IV)-(V), Co(I)-(II)-(III), Ti(II)-(III)-(IV), V(II)-(III)-(IV)-(V), Mo(II)-(III)-(IV)-(V)-(VI) and W(IV)-(V)-(VI);

X represents a coordinating species selected from any mono, bi or tri charged anions and any neutral molecules able to coordinate the metal in a mono, bi or tridentate manner;

Y represents any non-coordinated counter ion;

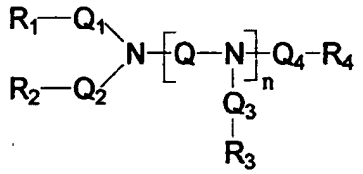
a represents an integer from 1 to 10;

k represents an integer from 1 to 10;

n represents an integer from 1 to 10;

m represents zero or an integer from 1 to 20; and

L represents a ligand of the general formula (I), or its protonated or deprotonated analogue:



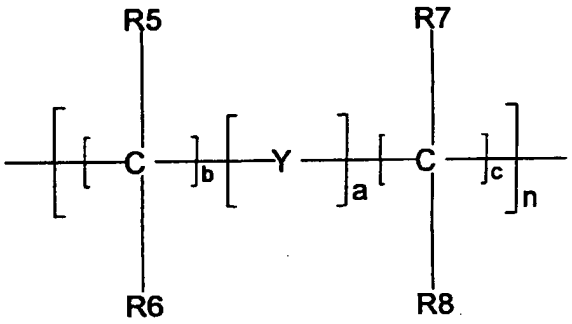
(I)

wherein

n = 1 or 2, whereby if n = 2, then each $-Q_3-R_3$ group is independently defined;

R_1, R_2, R_3, R_4 independently represent a group selected from hydrogen, hydroxyl, halogen, $-NH-C(NH)NH_2$, -R and -OR, wherein R= alkyl, alkenyl, cycloalkyl. heterocycloalkyl, aryl, heteroaryl or a carbonyl derivative group, R being optionally substituted by one or more functional groups E,

Q_1, Q_2, Q_3, Q_4 and Q independently represent a group of the formula:



wherein

$5 \geq a+b+c \geq 1$; a=0-5; b=0-5; c=0-5; n=1 or 2;

Y independently represents a group selected from -O-, -S-, -SO-, $-SO_2-$, -C(O)-, arylene, alkylene, heteroarylene, heterocycloalkylene, -(G)P-, -P(O)- and -(G)N- , wherein G is selected from hydrogen, alkyl, aryl, arylalkyl, cycloalkyl, each except hydrogen being optionally substituted by one or more functional groups E;

R5, R6, R7, R8 independently represent a group selected from hydrogen, hydroxyl, halogen, -R and -OR, wherein R represents alkyl, alkenyl, cycloalkyl,

heterocycloalkyl, aryl, heteroaryl or a carbonyl derivative group, R being optionally substituted by one or more functional groups E,

or R5 together with R6, or R7 together with R8, or both, represent oxygen.

or R5 together with R7 and/or independently R6 together with R8, or R5 together with R8 and/or independently R6 together with R7, represent C_{1-6}-alkylene optionally substituted by C_{1-4}-alkyl, -F, -Cl, -Br or -I; and

E independently represents a functional group selected from -F, -Cl, -Br, -I, -OH, -OR', $-NH_2$, -NHR', $-N(R')_2$, $-N(R')_3^+$, -C(O)R', -OC(O)R', -COOH, $-COO^-(Na^+, K^+)$, -COOR', $-C(O)NH_2$, -C(O)NHR', $-C(O)N(R')_2$, heteroaryl, -R', -SR', -SH, $-P(R')_2$, $-P(O)(R')_2$, $-P(O)(OH)_2$, $-P(O)(OR')_2$, $-NO_2$, $-SO_3H$, $-SO_3^-(Na^+, K^+)$, $-S(O)_2R'$, -NHC(O)R', and -N(R')C(O)R', wherein R' represents cycloalkyl, aryl, arylalkyl, or alkyl optionally substituted by -F, -Cl, -Br, -I, $-NH_3^+$, $-SO_3H$, $-SO_3^-(Na^+, K^+)$, -COOH, $-COO^-(Na^+, K^+)$, $-P(O)(OH)_2$, or $-P(O)(O^-(Na^+, K^+))_2$,

provided that at least two of R_1, R_2, R_3, R_4 comprise coordinating heteroatoms and no more than six heteroatoms are coordinated to the same transition metal atom.

2. A bleaching composition according to claim 1, wherein the medium has a pH value in the range from pH 6 to 11, preferably in the range from pH 8 to 10.

3. A bleaching composition according to claim 1 or claim 2, wherein the medium is substantially devoid of a transition metal sequestrant.

4. A bleaching composition according to any of claims 1 to 3, wherein the medium further comprises a surfactant.

5. A bleaching composition according to any of claims 1 to 4, wherein the medium further comprises a builder.

6. A bleaching composition according to any of claims 1 to 5, wherein the composition comprises a preformed complex of the ligand and a transition metal.

7. A bleaching composition according to any of claims 1 to 5, wherein the ligand is present as a free ligand that complexes with a transition metal present in the water.

8. A bleaching composition according to any of claims 1 to 5, wherein the ligand is present as a free ligand that complexes with a transition metal present in the substrate.

9. A bleaching composition according to any of claims 1 to 5, wherein the composition comprises the ligand present as a free ligand or a transition metal-substitutable metal-ligand complex, and a source of transition metal.

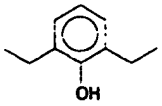
10. A bleaching composition according to any preceding claim, wherein at least two of R_1, R_2, R_3, R_4 independently represent a group selected from carboxylate, amido, -NH-C(NH)NH_2, hydroxyphenyl, an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole.

11. A bleaching composition according to any preceding claim, wherein R5, R6, R7, R8 independently represent a group selected from -H, hydroxy-C_0-C_{20}-alkyl, halo-C_0-C_{20}-alkyl, nitroso, formyl-C_0-C_{20}-alkyl, carboxyl-C_0-C_{20}-alkyl and esters and salts thereof, carbamoyl-C_0-C_{20}-alkyl, sulfo-C_0-C_{20}-alkyl and esters and salts thereof, sulfamoyl-C_0-C_{20}-alkyl, amino-C_0-C_{20}-alkyl, aryl-C_0-C_{20}-alkyl, C_0-C_{20}-alkyl, alkoxy-C_0-C_8-alkyl, carbonyl-C_0-C_6-alkoxy, and C_0-C_{20}-alkylamide.

12. A bleaching composition according to any preceding claim, wherein Q_1, Q_2, Q_3, Q_4 independently represent a group selected from -CH_2- and -CH_2CH_2-.

13. A bleaching composition according to any preceding claim, wherein Q represents a group selected from $-(CH_2)_{2-4}-$, $-CH_2CH(OH)CH_2-$,

 optionally substituted by methyl or ethyl,



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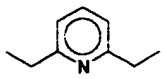
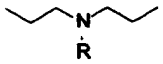
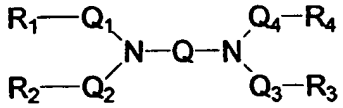


, and


wherein R represents -H or C_{1-4}-alkyl.

14. A bleaching composition according to any preceding claim, wherein Q_1, Q_2, Q_3, Q_4 are defined such that a=b=0, c=1 and n=1, and Q is defined such that a=b=0, c=2 and n=1.

15. A bleaching composition according to any preceding claim, wherein the ligand L is of the general formula (II):



(II)

wherein

Q_1, Q_2, Q_3, Q_4 are defined such that a=b=0, c=1 or 2 and n=1;

Q is defined such that a=b=0, c=2,3 or 4 and n=1; and

R_1, R_2, R_3, R_4, R7, R8 are independently defined as for formula (I).

16. A bleaching composition according to claim 15, wherein the ligand L is of the general formula (II) wherein

R_1, R_2, R_3, R_4 each independently represent a coordinating group selected from carboxylate, amido, $-NH-C(NH)NH_2$, hydroxyphenyl, an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine,

pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole. oxazole and thiazole.

17. A bleaching composition according to claim 16, wherein

Q is defined such that a=b=0, c=2 or 3 and n=1;

R_1, R_2, R_3, R_4 each independently represent a coordinating group selected from optionally substituted pyridin-2-yl, optionally substituted imidazol-2-yl, optionally substituted imidazol-4-yl, optionally substituted pyrazol-1-yl, and optionally substituted quinolin-2-yl.

18. A bleaching composition according to claim 15, wherein the ligand L is of the general formula (II) wherein

R_1, R_2, R_3 each independently represent a coordinating group selected from carboxylate, amido, -NH-C(NH)NH_2, hydroxyphenyl, an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole; and

R_4 represents a group selected from hydrogen, $C_{1\text{-}20}$ optionally substituted alkyl, $C_{1\text{-}20}$ optionally substituted arylalkyl, aryl, and $C_{1\text{-}20}$ optionally substituted NR_3^+ (wherein R=$C_{1\text{-}8}$-alkyl).

19. A bleaching composition according to claim 18, wherein

Q is defined such that a=b=0, c=2 or 3 and n=1;

R_1, R_2, R_3 each independently represent a coordinating group selected from optionally substituted pyridin-2-yl, optionally substituted imidazol-2-yl, optionally substituted imidazol-4-yl, optionally substituted pyrazol-1-yl, and optionally substituted quinolin-2-yl; and

R_4 represents a group selected from hydrogen, $C_{1\text{-}10}$ optionally substituted alkyl, $C_{1\text{-}5}$-furanyl, $C_{1\text{-}5}$ optionally substituted benzylalkyl, benzyl, $C_{1\text{-}5}$ optionally substituted alkoxy, and $C_{1\text{-}20}$ optionally substituted N^+Me_3.

20. A bleaching composition according to claim 15, wherein the ligand L is of the general formula (II) wherein:

R_1, R_4 each independently represent a coordinating group selected from carboxylate, amido, -NH-C(NH)NH_2, hydroxyphenyl, an optionally substituted heterocyclic ring or an optionally substituted heteroaromatic ring selected from pyridine, pyrimidine, pyrazine, pyrazole, imidazole, benzimidazole, quinoline, quinoxaline, triazole, isoquinoline, carbazole, indole, isoindole, oxazole and thiazole; and

R_2, R_3 each independently represent a group selected from hydrogen, C_{1-20} optionally substituted alkyl, C_{1-20} optionally substituted arylalkyl, aryl, and C_{1-20} optionally substituted NR_3^+ (wherein R=C_{1-8}-alkyl).

21. A bleaching composition according to claim 20, wherein:

Q is defined such that a=b=0, c=2 or 3 and n=1;

R_1, R_4 each independently represent a coordinating group selected from optionally substituted pyridin-2-yl, optionally substituted imidazol-2-yl, optionally substituted imidazol-4-yl, optionally substituted pyrazol-1-yl, and optionally substituted quinolin-2-yl; and

R_2, R_3 each independently represent a group selected from hydrogen, C_{1-10} optionally substituted alkyl, C_{1-5}-furanyl, C_{1-5} optionally substituted benzylalkyl, benzyl, C_{1-5} optionally substituted alkoxy, and C_{1-20} optionally substituted N^+Me_3.

22. A bleaching composition according to any preceding claim, wherein the composition comprises a mixture of the ligand L and a metal salt MX_n in which n=1-5, preferably 1-3.

23. A method of bleaching a substrate comprising applying to the substrate, in an aqueous medium, a ligand which forms a complex with a transition metal, the complex catalysing bleaching of the substrate by atmospheric oxygen, wherein the ligand is as defined in any of claims 1 to 21.

24. A method according to claim 23, wherein the majority of the bleaching species in the medium (on an equivalent weight basis) is derived from the atmospheric oxygen.

25. A method according to claim 23 or claim 24, wherein the medium is substantially devoid of peroxygen bleach or a peroxy-based or -generating bleach system.

26. A method according to any of claims 23 to 25, wherein the aqueous medium is agitated.

27. A method according to any of claims 23 to 26, wherein the medium is as defined in any of claims 2 to 5.

28. Use of a ligand which forms a complex with a transition metal as a catalytic bleaching agent for a substrate in an aqueous medium substantially devoid of peroxygen bleach or a peroxy-based or -generating bleach system, the complex catalysing bleaching of the substrate by the atmospheric oxygen wherein the ligand is as defined in any of claims 1 to 21.

29. A method of treating a textile by contacting the textile with a ligand which forms a complex with a transition metal, whereby the complex catalyses bleaching of the textile by atmospheric oxygen after the treatment, wherein the ligand is as defined in any of claims 1 to 21.

30. A method according to claim 29, wherein the treatment comprises contacting the textile with the ligand in dry form.

31. A method according to claim 30, wherein the treatment comprises contacting the textile with a liquor containing the ligand and then drying.

32. A method according to claim 31, wherein the liquor is an aqueous liquor.

33. A method according to claim 32, wherein the liquor is a spray-on fabric treatment fluid.

34. A method according to claim 32, wherein the liquor is a wash liquor for laundry cleaning.

35. A method according to claim 31, wherein the liquor is a non-aqueous liquor.

36. A method according to claim 35, wherein the liquor is a dry cleaning fluid.

37. A method according to claim 35, wherein the liquor is a spray-on aerosol fluid.

38. A method according to any of claims 31 to 37, wherein the liquor is substantially devoid of peroxygen bleach or a peroxy-based or -generating bleach system.

39. A dry textile having a ligand as defined in any of claims 1 to 21 applied or deposited thereon, whereby bleaching by atmospheric oxygen is catalysed on the textile.

40. A ligand selected from:
N,N,N',N'-tetrakis(3-methyl-pyridin-2-ylmethyl)-ethylene-diamine; and
N,N'-dimethyl-N,N'-bis(pyridin-2-ylmethyl)-cyclohexane-1,2-diamine.

41. A complex comprising a ligand as defined in claim 40.

INTERNATIONAL SEARCH REPORT

Inter. nal Application No
PCT/EP 00/02587

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/395 C07D213/38 C07F15/02 C07F13/00 D06L3/02
C07D235/30 C07D405/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D C07D C07F D06L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95 34628 A (UNILEVER NV ;UNILEVER PLC (GB)) 21 December 1995 (1995-12-21) cited in the application claims	1-41
A	DE 197 14 122 A (CLARIANT GMBH) 8 October 1998 (1998-10-08) claims	1-41
A	WO 95 27772 A (PROCTER & GAMBLE) 19 October 1995 (1995-10-19) claims	1-41
A	WO 97 48787 A (UNILEVER PLC ;UNILEVER NV (NL)) 24 December 1997 (1997-12-24) cited in the application claims	1-41

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
6 July 2000	18/07/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Chouly, J

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INTERNATIONAL SEARCH REPORT

Inter. nal Application No
PCT/EP 00/02587

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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P,Y	WO 00 12808 A (UNILEVER PLC ;LEVER HINDUSTAN LTD (IN); UNILEVER NV (NL)) 9 March 2000 (2000-03-09) claims	1-41

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